

REMARKS

With entry of the present amendment, the application will contain claims 1-22, all of which are under examination. Claim 6 has been rewritten to be independent and is now clearly allowable.

Allowable Subject Matter

The Examiner is thanked for the indication in the second and third full paragraphs on page 3 of the last Office Action of the allowability of a number of claims. Claim 6 has been rewritten to be independent and is now clearly allowable. Claims 8 and 10-13 are objected to only because they depend from a rejected base claim. As explained more completely below, the rejected base claim should be allowable. Accordingly, these claims should all be allowable.

The Examiner stated "claim 22 appears to be allowable". Claim 22 is independent. The Examiner is respectfully requested to allow this claim.

Amendments to the Specification

The only amendments to the specification are minor amendments in wording that occurs in Tables 1 and 2, which appear respectively on pages 59 and 60. The phrase "Mw" has been replaced by the phrase "a molecular weight". These minor amendments to Tables 1

and 2 do not introduce any new matter into the specification. Claim 1 as filed employs the phrase "a molecular weight". The same phrase appears in the specification page 3 at line 11; page 10 at line 5; page 50 at line 21; page 51 at line 2; page 51 at line 2; and page 51 at line 13.

Issues Under 35 USC § 112

The rejection of claims 1-20 under the second paragraph of 35 USC § 112 is traversed. The phrase "a molecular weight" is completely appropriate and proper under the circumstances of the present invention.

The phrase "a molecular weight", in claim 1, is neither a number average molecular weight nor a weight average molecular weight.

In general, aggregates of polymers are mixtures of different-sized molecules. Both the number average molecular weight and the weight average molecular weight are average values of the molecular weight of the mixture, that is a kind of representative value of the mixture of different-sized molecules. Further, each (polymer) molecule which forms the mixture also has a molecular weight. This is a matter of common knowledge for a person of ordinary skill in the art and is described in a number of references such as Rodriguez' "PRINCIPLES OF POLYMER SYSTEM" attached hereto as

Exhibit A. In claim 1, "molecular weight" means the molecular weight of each polymer molecule which is represented as " M_i " by Rodriguez.

Defining the molecular weight in claim 1 with the number average molecular weight or the weight average molecular weight would be strange, and would be inconsistent with the common knowledge.

As explained above, it is clear to a person of ordinary skill in the art that "molecular weight" in claim 1 is neither the number average molecular weight nor the weight average molecular weight, but the molecular weight. Therefore, "...the polyphenylene ether resin in the composition contains 10 to 30 wt.% of polymer having a molecular weight of 20,000 or less..." in claim 1 is definite and complies with both the letter and the spirit of 35 USC § 112.

The attention of the Examiner is respectfully invited to the "CHART" attached as Exhibit B. Exhibit B graphically explains the meaning of "molecular weight". In the chart, the horizontal scale (x) and a vertical scale (y) respectively represent the molecular weight (M_i) and the number of molecules of molecular weight M_i (N_i). A curve therein represents a distribution of molecular weights. An area of shaded portion therein corresponds to a content of the polymer having a molecular weight of 20,000 or less. In claim 1, the phrase "...the polyphenylene ether resin..." contains

10 to 30 wt.% of polymer having a molecular weight of 20,000 or less..." means that the area of shaded portion is 10 to 30% of an area of portion surrounded by the curve and a horizontal line of $Ni=0.0$.

Issues Under 35 USC § 103

The rejection of claims 1-5, 7, 9 and 14-21 as obvious under 35 USC § 103 over WO 01/81471 (The World Patent) in view of EP0 997 495 (The EP reference) is traversed on multiple grounds. First, it is respectfully submitted that the world patent is simply not a reference against the present application. Even if the world patent is a reference, it would not be obvious to combine the teachings of the world patent and the EP reference in the manner suggested by the Examiner. Third, even presuming that the world patent is a reference and even presuming the obviousness of the combination of the world patent and the EP reference, the result of such a theoretical hypothetical combination would still not be the subject matter claimed. Fourth, unexpected results inherent in the present invention clearly indicate its patentability over all cited references either alone or in combination.

The present invention and its Advantages

The present invention is concerned with providing a resin composition comprising a polyphenylene ether resin and a liquid-crystal polyester. Claim 1 defines a resin composition comprising (A) 70 to 99 parts by weight of a polyphenylene ether resin, and (B) 1 to 30 parts by weight of a liquid-crystal polyester, wherein the polyphenylene ether resin in the composition contains 10 to 30 wt.% of polymer having a molecular weight of 20,000 or less and has a molecular weight distribution (Mw/Mn) of 1.8 to 3.5.

As described in SUMMARY OF THE INVENTION of the instant specification at pages 2-3, according to the present invention, the resin composition can simultaneously attain excellent impact strength, chemical resistance, heat resistance and flame retardancy and fluidity.

Distinctions Over the Cited Art

(1) The World Patent

The World Patent is not a reference.

The publication date of the World Patent is November 1, 2001. On the other hand, the filing date of the present application is March 4, 2002.

However, the present application has claimed the foreign priorities based on Japanese applications having filing dates of March 8 and September 6, 2001.

Therefore, the World Patent can be antedated by perfecting claims to the priorities.

Certified translations of the Japanese priority applications are attached hereto as Exhibits C and D.

(2) The EP Reference

In the EP reference, there is provided a thermoplastic resin composition comprising a polyphenylene ether resin and a liquid crystalline polymer.

However, the EP reference neither teaches nor suggests in any way "the polyphenylene ether resin in the composition contains 10 to 30 wt.% of polymer having a molecular weight of 20,000 or less, having a molecular weight distribution (Mw/Mn) of 1.8 to 3.5". Instead, the EP reference simply and generally describes polyphenylene ether resin at claim 1, paragraphs 0039-0041, 0113 and Examples 14-15 and 25 (see Tables 1 and 2), giving no specific explanation about either molecular weight or molecular weight distribution.

Furthermore, the present invention is completely different from the EP reference in a fundamental way to improve a

polyphenylene ether resin composition. In the EP reference, it is described that some additives are added to polyphenylene ether resin so that some properties can be improved. In Examples 14-15 and 25, impact strength, heat resistance, flowability and chemical resistance and fluidity of a polyphenylene ether resin composition are evaluated. However, with respect to flame retardancy, flame retardant such as a phosphorus compound is added so as to impart flame retardancy (see paragraph 0076).

By contrast, in the present invention, the polyphenylene ether resin itself is specified so as to improve flame retardancy as well as other properties. The technological way of obtaining excellent properties in the present invention is completely different from that of the EP reference.

Therefore, the EP reference neither teaches nor suggests in any way the specific resin composition being claimed, and provides no motivation to arrive at the same and fails to recognize the unexpected results that are associated therewith.

Unexpected Results

The present invention, moreover, shows unexpected results over the prior art.

In the EP reference, impact strength, chemical resistance, flowability (fluidity) and heat resistance are mentioned regarding

a resin composition comprising a general polyphenylene ether resin and a liquid crystalline polymer (see Tables 1 and 2). However, flame retardancy is imparted by adding a flame retardant (see paragraph 0076). Further, any flame retardancy was not evaluated specifically in the Examples of the reference.

By contrast, the present invention simultaneously attains excellent impact strength, flame retardancy, chemical resistance, heat resistance and fluidity by employing the specified polyphenylene ether resin as well as a liquid-crystal polyester.

The attention of the Examiner is respectfully invited to the "CHART OF PROPERTIES" attached hereto as Exhibit E. Exhibit E visually shows an excellent balance in those properties using evaluations of Example 1 and Comparative Examples 1-3. As shown on Exhibit E, it is clear that the compositions of the present invention have an excellent balance.

Each numerical value shown on Exhibit E represents as follows:

With respect to impact strength, chemical resistance and heat resistance

Each numerical value shown on Exhibit B represents a relative numerical value converted from an actual evaluation at each property of Example 1 and Comparative Examples 1-3 where each evaluation of properties of Example 1 is defined as 100.

With respect to chemical resistance of Comparative Examples 2 and 3, a specimen therein was broken when pulled out from the solution (see "X" at chemical resistance of Examples 2 and 3 in Table 1 of the instant specification). Therefore, chemical resistance of Comparative Examples 2 and 3 is "0" (zero).

With respect to fluidity

Unlike Izod impact strength, chemical strength and heat resistance, smaller SSP value is preferable. So, SSP value itself has to be converted so that the evaluation thereof can be shown visually on Exhibit E. Conversion is conducted using each reciprocal of SSP value.

Namely, each numerical value of fluidity shown on Exhibit B represents a relative numerical value, which is calculated using each reciprocal of SSP value of Comparative Examples 1-3, where "100 X reciprocal of SSP value of Example 1" is defined as 100.

More specifically, each numerical value of fluidity shown on Exhibit B is calculated using the following formula.

Numerical value of fluidity = 100 X SSP value of Example 1/SSP value (of Example 1 or Comparative Examples 1-3).

With respect to flame retardancy

Like the SSP value, a shorter average combustion time is preferable. So, an average combustion time itself has to be converted so that the evaluation thereof can be shown visually on Exhibit B. Conversion is conducted using reciprocal of average combustion time.

Namely, each numerical value of flame retardancy shown on Exhibit B represents relative numerical value, which is calculated using each reciprocal of average combustion time of Comparative Examples 1, 2 or 3, wherein "100 X reciprocal of average combustion time of Example 1" are defined as 100.

More specifically, each numerical value of flame retardancy shown on Exhibit B is calculated by the following formula.

Numerical value of flame retardancy = 100 X an average combustion time of Example 1/an average combustion time (of Example 1 or Comparative Examples 1-3).

CONCLUSION

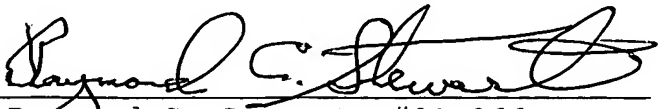
As mentioned above, the World Patent is not a reference against the present application, and the EP reference neither teaches nor suggests any motivation to arrive at the present invention. Furthermore, the present invention shows unexpected results over the prior art and is patentable over the cited references.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact David R. Murphy (Reg. No. 22,751) at the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. §§ 1.16 or 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By 
Raymond C. Stewart, #21,066

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Exhibits:

A. Rodriguez; "PRINCIPLES OF POLYMER SYSTEMS" Hemisphere Publishing Corp.; Washington DC, USA; 1996; (Cover, frontispiece and pages 187-190 inclusive; a total of 6 pages)

B. "CHART OF MOLECULAR WEIGHT" (1 page)

C. Certified translation of first priority document (2001-064678)

D. Certified translation of second priority document (2001-270006)

E. "CHART OF MOLECULAR WEIGHT" (1 page)

PRINCIPLES OF POLYMER SYSTEMS

Ferdinand Rodriguez



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CHAPTER
SIX

THE MOLECULAR WEIGHT OF POLYMERS

6.1 AVERAGE MOLECULAR WEIGHT

The high molecular weight of polymers is responsible for many of the properties that make polymers valuable as a class of materials. Although there is no sharp dividing line, we can draw an imaginary one at a molecular weight of about 2000, since that is near the limit of convenient purification by distillation or extraction. Also, differences between members of a homologous series differing in steps of 100 or so (the molecular weight of a typical monomer) become so slight as to prevent clean separations. Some polymers, such as polyethylene, poly(ethylene oxide), and dimethyl silicones, are commercially available in sizes ranging almost continuously from monomer or dimer up to molecular weights in the millions. Except for the smaller members of each series, each of these products is a mixture of different-sized molecules having an *average molecular weight*, which we can define and measure in several ways, and a *distribution* of molecular weights. Distributions used to be rather tedious to measure and not as often specified as the average molecular weight. However, chromatographic techniques changed this situation.

If someone told you that he wanted to drop into your hand, from a height of 1 ft, a series of 1000 steel balls with an average diameter of 2.4 in, you might agree to help him in his playful experiment. After all, a 2.4-in diameter steel ball weighs only about 2 lb. However, if he said the average diameter was 23.6 in, your attitude might be less cooperative. Both numbers could refer to the same series of balls, the difference being in the manner in which the "average" diameter is calculated. If

188 PRINCIPLES OF POLYMER SYSTEMS

Table 6.1 Hypothetical distribution f balls

Number of balls N_i	Diameter D_i , in	Length $N_i D_i$	Area ($\times 1/\pi$) $N_i D_i^2$	Volume ($\times 6/\pi$) $N_i D_i^3$
900	1	900	900	900
50	5	250	1,250	6,250
50	25	1250	31,250	781,250
$\Sigma N_i = 1000$		$\Sigma N_i D_i = 2400$	$\Sigma = 33,400$	$\Sigma = 788,400$

the population is as shown in Table 6.1, we can calculate an average diameter in several ways:

The average diameter \bar{D}_L , based on length (one dimension):

$$\bar{D}_L = \frac{\Sigma N_i D_i}{\Sigma N_i} = \frac{2400}{1000} = 2.4 \text{ in}$$

The average diameter \bar{D}_A , based on area (two dimensions):

$$\bar{D}_A = \frac{\Sigma N_i D_i^2}{\Sigma N_i D_i} = \frac{33,400}{2400} = 13.9 \text{ in}$$

The average diameter \bar{D}_V , based on volume (three dimensions):

$$\bar{D}_V = \frac{\Sigma N_i D_i^3}{\Sigma N_i D_i^2} = \frac{788,400}{33,400} = 23.6 \text{ in}$$

Although \bar{D}_L reflects the preponderant number of small balls, the 1-in balls represent only about 0.1% of the total volume. \bar{D}_V reflects the importance of the few large balls, which represent 99% of the volume (and weight) of the system. Incidentally, each 25-in ball weighs about 1 ton.

Let us now imagine a population of polymers with molecular weights distributed as in Table 6.1, where N is now the number of molecules of molecular weight $M = D$. The quantity we called $N_i D_i$ before is now $N_i M_i = W_i$, the weight of species with molecular weight M_i . We have used before the concept of a number-average molecular weight M_n , where

$$M_n = \frac{\text{total weight of system}}{\text{molecules in system}} \quad (6.1)$$

In terms of any population, then,

$$M_n = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{\Sigma W_i}{\Sigma (W_i/M_i)} \quad (6.2)$$

As in the case of the steel balls, M_n is very sensitive to the concentration of low-molecular-weight species. The weight-average molecular weight M_w is defined as

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum W_i M_i}{\sum W_i} \quad (6.3)$$

In correlating such important polymer properties as viscosity or toughness, M_w often is a more useful parameter than M_n . Higher averages are defined as

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum W_i M_i^2}{\sum W_i M_i} \quad (6.4)$$

$$M_{z+1} = \frac{\sum N_i M_i^4}{\sum N_i M_i^3} = \frac{\sum W_i M_i^3}{\sum W_i M_i^2} \quad (6.5)$$

These are used less often than M_n and M_w . The ratio of M_w to M_n is a measure of the broadness of a distribution, since each is influenced by an opposite end of the population. The quantity M_w/M_n is the *polydispersity index* (PDI).

Example 6.1

A polymer shipment is to be made up by blending three lots of polyethylene, A, B, and C. How much of each lot is needed to make up a shipment of 50,000 kg with a weight-average molecular weight of 250,000 and a polydispersity index (PDI) of 3.65? Let $w_i = W_i/\sum W_i$

Lot	M_w	PDI
A	500,000	2.50
B	250,000	2.00
C	125,000	2.50

Solution:

$$\begin{aligned} M_w &= \sum w_i (M_w)_i \\ 250,000 &= 500,000w_A + 250,000w_B + 125,000(1 - w_A - w_B) \\ 2.50 &= 5.00w_A + 2.50w_B + 1.25(1 - w_A - w_B) \\ w_A &= 0.333 - 0.333w_B \\ \frac{1}{M_n} &= \sum \frac{w_i}{(M_n)_i} \end{aligned}$$

(For convenience, divide molecular weights by 1000.)

$$\text{Each } (M_n)_i = \left(\frac{M_w}{\text{PDI}} \right)_i$$

190 PRINCIPLES OF POLYMER SYSTEMS

$$\frac{1}{68.5} = \frac{w_A}{200} + \frac{w_B}{125} + \frac{1 - w_A - w_B}{50}$$

$$w_A = 0.360 - 0.800w_B$$

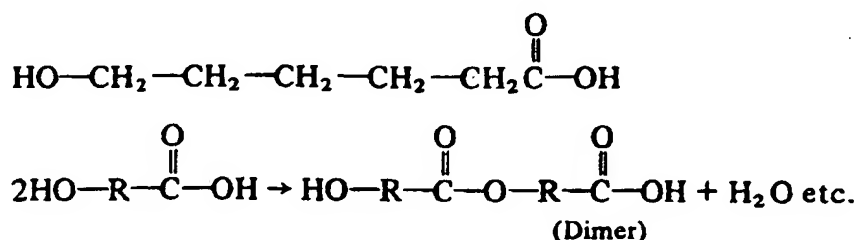
Solve simultaneously:

$$w_A = 0.058 \quad w_B = 0.314 \quad w_C = 0.628$$

Amounts needed are 2,900 kg A, 15,700 kg B, and 31,400 kg C.

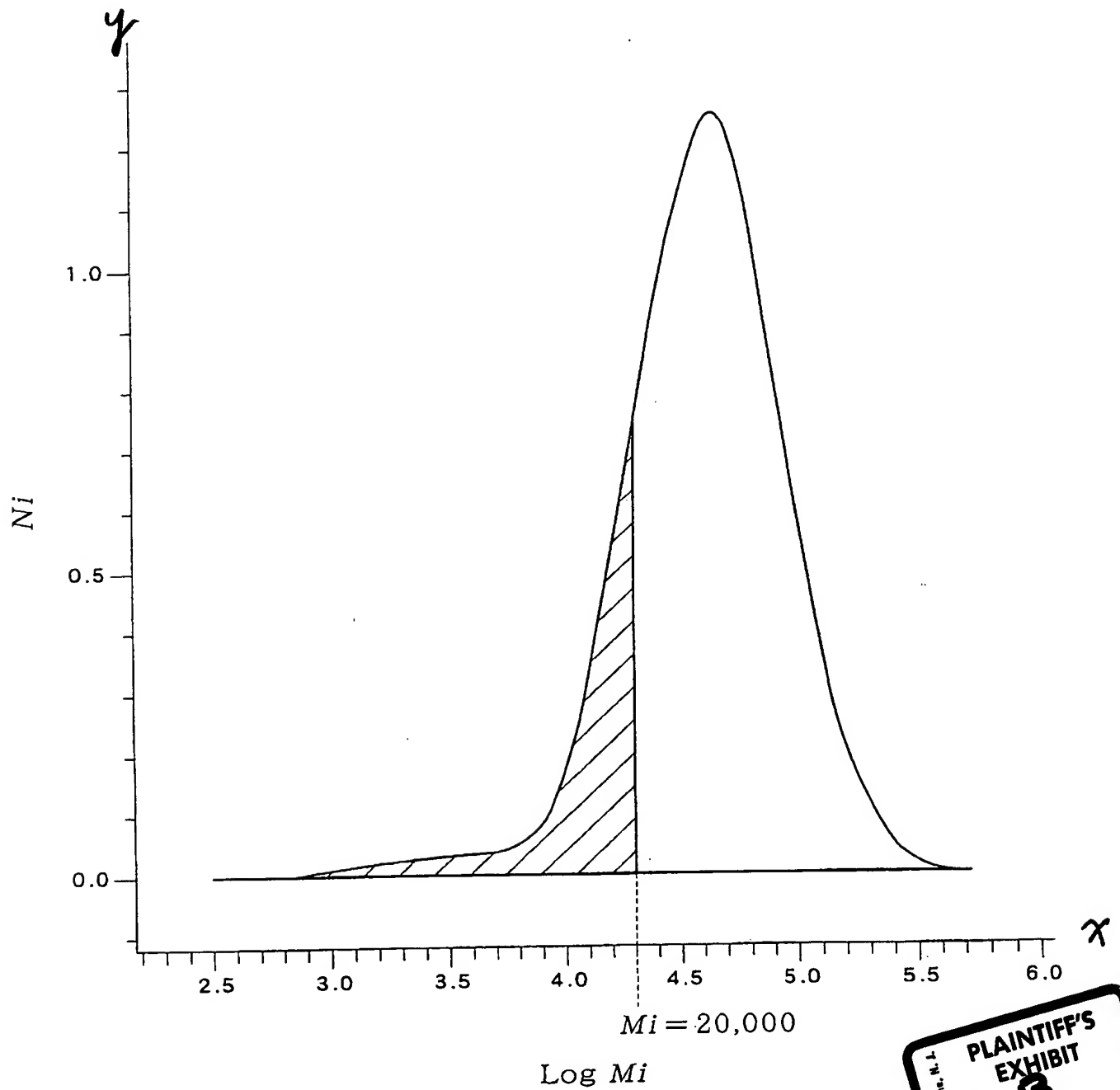
6.2 THEORETICAL DISTRIBUTIONS

With the possible exception of some naturally occurring proteins, all polymers are mixtures of many molecular weights ("polydisperse"). This is a consequence of the random nature of polymerization reactions. For example, take the case analyzed by Flory [1] in which the monomer is an ω -hydroxy acid (see also Sec. 4.7).



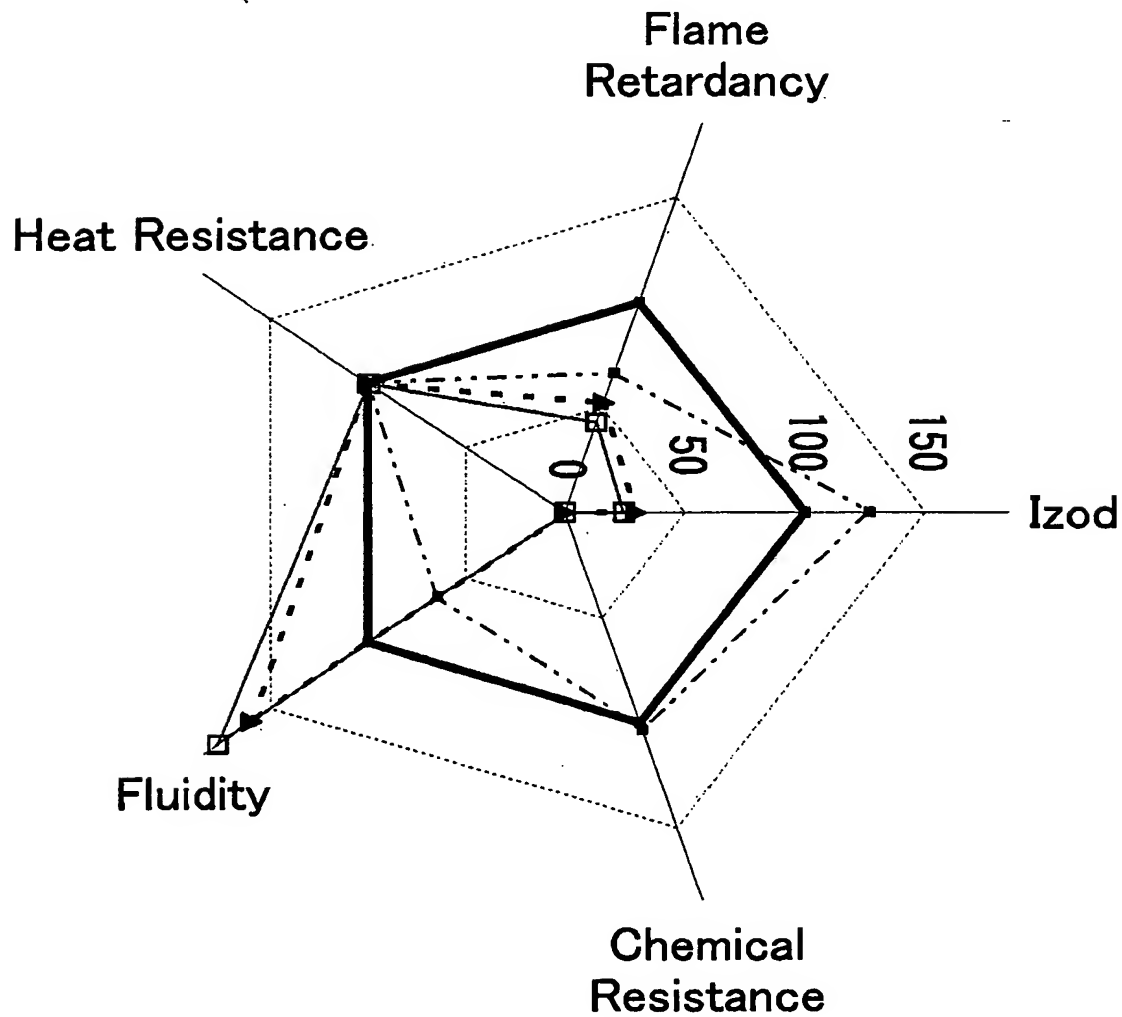
This is a typical stepwise polymerization in which each successively higher molecular weight, dimer, trimer, etc., is just as reactive as monomer. An important parameter is the fraction converted, p . If we have a population of such monomers, each can react to form an ester group. Each esterification eliminates one carboxyl and one hydroxyl group. With five monomers (Fig. 6.1) there would be a maximum of five esterifications ($p = 1$). Initially, p is 0. After one reaction, $p = 0.20$. Abbreviating the unreacted sites by the symbol U and the esterified sites by the symbol E , we can generate a distribution of molecular weights by random reaction of 50 out of 100 sites ($p = 0.5$). If we had alternated sites of reaction with unreacted sites, we would have generated 50 dimers and no other species. Another possible extreme would be to generate 49 monomers and 1 polymer molecule with a degree of polymerization x of 51. We have 50 molecules in either case. With random reaction (Fig. 6.1), monomers predominate in number of molecules N_x , although not necessarily in weight xN_x . If our sample population were much larger, as it is in any macroscopic polymerization, we could assign a probability $(P)_x$ that a monomer unit selected at random is a part of a polymer with degree of polymerization x . We expect this to be a function of p , which is the probability that any particular reactive site has been esterified. The probability that a monomer unit is still unreacted varies from 1 when $p = 0$ to 0 when $p = 1$. We surmise that

CHART OF MOLECULAR WEIGHT



PENGAD-349000, N. 1
**PLAINTIFF'S
EXHIBIT**
B

CHART OF PROPERTIES



—■— EX1
-▲- COM1
-●- COM2
-□- COM3

PLAINTIFF'S
EXHIBIT
E

VERIFIED TRANSLATION

I, Rei Terasaki, hereby declare that:

I am knowledgeable in Japanese and English. I have reviewed the attached document and believe it to be an accurate translation of Japanese Patent Application No. 2001-064678 filed on March 8, 2001.

All statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true. Further, these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: Nov. 5, 2003

Rei Terasaki

Rei Terasaki



[NAME OF DOCUMENT] Application for Patent
[REFERENCE NUMBER] X13-00262
[FILING DATE] March 8, 2001
[SUBMITTED TO] Commissioner, Patent Office
[INTERNATIONAL PATENT CLASSIFICATION]
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C08L 67/03
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[LIST OF MATERIALS TO BE SUBMITTED]
[NAME OF MATERIAL] Abstract
[NUMBER OF MATERIAL] 1
[NECESSITY FOR PROOF] 1: Necessary to prove

[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

A Resin Composition

[SCOPE OF PATENT]

[Claim 1]

A resin composition comprising:

(A) 30 to 99 parts by weight of a polyphenylene ether resin, and
(B) 1 to 70 parts by weight of a liquid-crystal polyester,
wherein the polyphenylene ether resin in the composition contains 5 to
30 wt.% of polymer having a molecular weight of 20,000 or less and has
a molecular weight distribution (Mw/Mn) of 1.8 to 3.5.

[Claim 2]

The resin composition according to claim 1, wherein component (A)
is contained in an amount of 70 to 99 parts by weight and component (B)
is contained in an amount of 1 to 30 parts by weight.

[Claim 3]

The resin composition according to claim 1 or 2, wherein (C) an
inorganic filler is added in an amount of 0.1 to 200 parts by weight based
on 100 parts by weight, in total, of components (A) and (B).

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a polyphenylene ether resin
composition which can simultaneously attain excellent impact resistance,
chemical resistance, fluidity, heat resistance and flame retardancy,
especially very excellent impact resistance, chemical resistance and
fluidity.

[0002]

[Prior Art]

In general, polyphenylene ethers are resins that have excellent
properties, for example, heat resistance, hot water resistance, size
stability and mechanical and electrical properties, but are accompanied
with drawbacks such as poor moldability owing to their high melt viscosity,
bad chemical resistance and low impact resistance. With a view to improving
such defects of polyphenylene ethers, methods of alloying polyphenylene
ether with another resin and modifying polyphenylene ethers have
conventionally been conducted.

[0003]

It is well-known that adding polystyrene to the polyphenylene ethers improves the fluidity of the composition. However, there are problems, which are, for example, that adding polystyrene impairs the heat resistance and chemical resistance. As a technique related to alloying of a polyphenylene ether with another resin, for example, JP-A-56-115357 proposed a process of mixing polymers, for example, a polyphenylene ether with a liquid-crystal polyester, thereby improving the melt processability of the polyphenylene ether. This process, however, is not sufficient to improve the impact resistance, chemical resistance and fluidity. JP-A-2-97555 proposed a process of mixing a liquid-crystal polyester with various polyallylene oxides in order to improve solder heat resistance, and JP-A-6-122762 proposed a process of mixing an amine-modified polyphenylene ether with a liquid-crystal polyester. Neither process is sufficient for a balance of impact resistance, chemical resistance, fluidity, heat resistance and flame retardancy.

[0004]

[Problems to be Solved by the Invention]

An object of the invention is to provide a polyphenylene ether resin composition which can simultaneously attain excellent impact resistance, chemical resistance, fluidity, heat resistance and flame retardancy, especially very excellent impact resistance, chemical resistance and fluidity.

[0005]

[Means to Solve the Problems]

To achieve the object mentioned above, the present inventor carried out extensive investigations. As a result, it was found that a resin composition capable of simultaneously exhibiting impact resistance, chemical resistance, fluidity, heat resistance and flame retardancy at an excellent level, particularly being excellent in impact resistance, chemical resistance and fluidity, can be obtained by mixing a polyphenylene ether resin having a specific molecular weight distribution and containing a substance having a specific molecular weight with a liquid-crystal polyester at a specific ratio, leading to the completion of the invention.

[0006]

Namely, the present invention provides:

1. A resin composition comprising:

(A) 30 to 99 parts by weight of a polyphenylene ether resin, and
(B) 1 to 70 parts by weight of a liquid-crystal polyester,
wherein the polyphenylene ether resin in the composition contains 5 to 30 wt.% of polymer having a molecular weight of 20,000 or less and has a molecular weight distribution (Mw/Mn) of 1.8 to 3.5.

2. The resin composition according to the above item 1, wherein component (A) is contained in an amount of 70 to 99 parts by weight and component (B) is contained in an amount of 1 to 30 parts by weight.

3. The resin composition according to the above item 1 or 2, wherein (C) an inorganic filler is added in an amount of 0.1 to 200 parts by weight based on 100 parts by weight, in total, of components (A) and (B).

[0007]

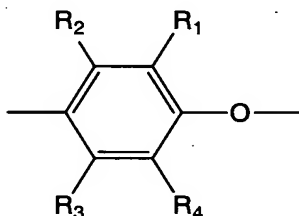
[Best Mode for Carrying Out the Invention]

Hereinafter, the present invention is described more specifically.

The polyphenylene ether resin (A) of the present invention is a homopolymer and/or copolymer comprising a recurring unit represented by the following formula (1):

[0008]

[Formula 1]



... (Formula 1)

[0009]

(wherein R1 and R4 each independently represents a hydrogen atom, a primary or secondary lower alkyl group, a phenyl group, and aminoalkyl group or a hydrocarbon oxy group; and R2 and R3 each independently represents a hydrogen atom, a primary or secondary lower alkyl group or a phenyl group), and

having a reduced viscosity (as measured under the condition: 0.5 g/dl, chloroform solution, and 30°C) of 0.15 to 1.0 dl/g. The reduced viscosity is more preferably within a range of 0.20 to 0.70 dl/g, most preferably within a range of 0.40 to 0.60 dl/g.

[0010]

Specific examples of the polyphenylene ether includes

poly(2,6-dimethyl-1,4-phenylene ether), poly(2-methyl-6-ethyl-1,4-phenylene ether), poly(2-methyl-6-phenyl-1,4-phenylene ether) and poly(2,6-dichloro-1,4-phenylene ether). The polyphenylene ether copolymers such as copolymers of 2,6-dimethylphenol and another phenol (such as 2,3,6-trimethylphenol or 2-methyl-6-butylphenol) can be also exemplified. Among them, poly(2,6-dimethyl-1,4-phenylene ether) and a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol are preferred, of which the poly(2,6-dimethyl-1,4-phenylene ether) is more preferred.

[0011]

Examples of a manufacturing process of the polyphenylene ether (A) to be used in the invention include the process described in U.S. Patent No. 3,306,874 wherein 2,6-xlenol is subjected to oxidation polymerization in the presence of complex comprising a cuprous salt and amine as a catalyst. The process described in U.S. Patent Nos. 3,306,875, 3,257,357 and 3,257,358, JP-B-52-17,880, JP-A-50-51,197 and JP-A-63-152,628 are also preferred as a manufacturing process of the polyphenylene ether (A).

[0012]

The polyphenylene ether resin (A) of the present invention may be used in the form of a powder produced after polymerization or in the form of pellets produced by melt kneading the powder of polyphenylene ether (A) with an extruder in the atmosphere of a nitrogen gas or non-nitrogen gas with or without deaeration.

Examples of the polyphenylene ether resin (A) of the present invention also include polyphenylene ethers functionalized with various dienophile compounds. Examples of various dienophile compounds include maleic anhydride, maleic acid, fumaric acid, phenyl maleimide, itaconic acid, acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, glycidyl acrylate, glycidyl methacrylate, stearyl acrylate and styrene. As the method for functionalizing the polyphenylene ether with dienophile compounds, functionalizing the polyphenylene in a molten state in the presence or absence of a radical generator by using an extruder, with or without deaeration, or functionalizing the polyphenylene in a non-molten state in the presence or absence of a radical generator, can be exemplified.

[0013]

The polyphenylene ether resin (A) in the present invention is a polyphenylene ether resin per se or a mixture comprising a polyphenylene ether resin and an aromatic vinyl polymer, which may further comprise

another resin. Examples of the aromatic vinyl polymer include atactic polystyrene, syndiotactic polystyrene, high impact polystyrene, an acrylonitrile-styrene copolymer and the like. When a mixture of a polyphenylene ether resin and an aromatic vinyl polymer is used, the amount of the polyphenylene ether resin is at least 70 wt.%, preferably at least 80 wt.%, more preferably at least 90 wt.% based on the total amount of the polyphenylene ether resin and aromatic vinyl polymer.

[0014]

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polyphenylene ether resin used in the present invention can be obtained in the following manner. The molecular weight of polyphenylene ether is determined by using a gel permeation chromatography apparatus ("HL-802 RTS", manufactured by Toyo Soda Co., Ltd.) and a working curve obtained from standard polystyrene samples. For the measurement, there are used standard polystyrene samples having a molecular weight of 264, 364, 466, 568, 2,800, 16,700, 186,000, 1,260,000, chromatographic columns ("TSK gel G2500H XL", "TSK gel G3000HXL", "TSK gel G4000HXL" and "TSK gel G5000HXL", manufactured by Toyo Soda Co., Ltd.) connected in series and chloroform as a solvent. The measurement is conducted at a solvent flow rate of 0.9 ml/min, and at a temperature of the columns of 40°C. The molecular weights of standard polystyrene and polyphenylene ether resin are measured using wavelengths of ultraviolet rays of 254 nm and 283 nm, respectively.

[0015]

The polyphenylene ether resin contained in the resin composition of the present invention may be obtained by dissolving pellets or a molded article comprising the resin composition in the chloroform at room temperature, removing insoluble material by filtration, charging the resultant solution in a sufficient amount of methanol to obtain precipitates, and washing the precipitates with methanol followed by drying under reduced pressure.

The molecular weight distribution (M_w/M_n) of the polyphenylene ether resin of the present invention is 1.8 to 3.5, preferably 2.0 to 3.4, more preferably 2.2 to 3.3. When it is less than 1.8, the fluidity is unpreferably decreased. When it is more than 3.5, the impact resistance and the chemical resistance are unpreferably reduced.

[0016]

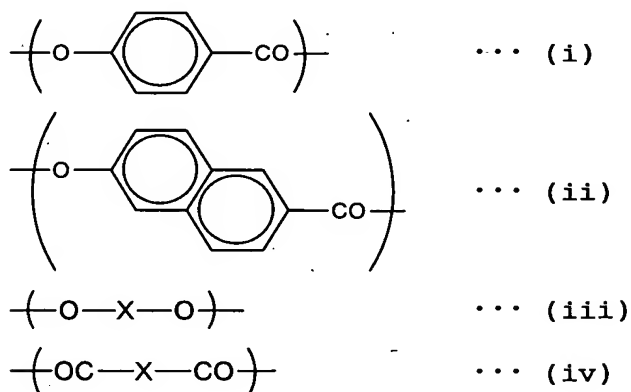
Further, the polyphenylene ether resin of the present invention contains a polymer having a molecular weight of 20,000 or less in an amount of 5 to 30 wt.%, preferably 10 to 25 wt.%, more preferably 12 to 24 wt.%. When the polymer having a molecular weight of 20,000 or less is contained in the above-described range, the composition of the present invention can exhibit excellent impact resistance, chemical resistance and fluidity, which are usually difficult to attain simultaneously, at a high level. When the content of the polymer having a molecular weight of 20,000 or less is less than 5 wt.%, the fluidity is considerably decreased. When it is more than 30 wt.%, the impact resistance and the chemical resistance are unpreferably decreased.

[0017]

As the liquid-crystal polyester (B) of the present invention, known polyesters called "thermotropic liquid-crystal polymers" can be used. Examples thereof include thermotropic liquid-crystal polyesters having, as a main constitutional unit, p-hydroxybenzoic acid and polyethylene terephthalate, thermotropic liquid-crystal polyesters having, as a main constitutional unit, p-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid, and thermotropic liquid-crystal polyesters having, as a main constitutional unit, p-hydroxybenzoic acid, 4,4'-dihydroxybiphenyl and terephthalic acid, but no particular limitation is imposed thereon. As the liquid-crystal polyester (B) to be used in the invention, those having the following structural units (i) and (ii), and optional (iii) and/or (iv) are preferably employed.

[0018]

[Formula 2]

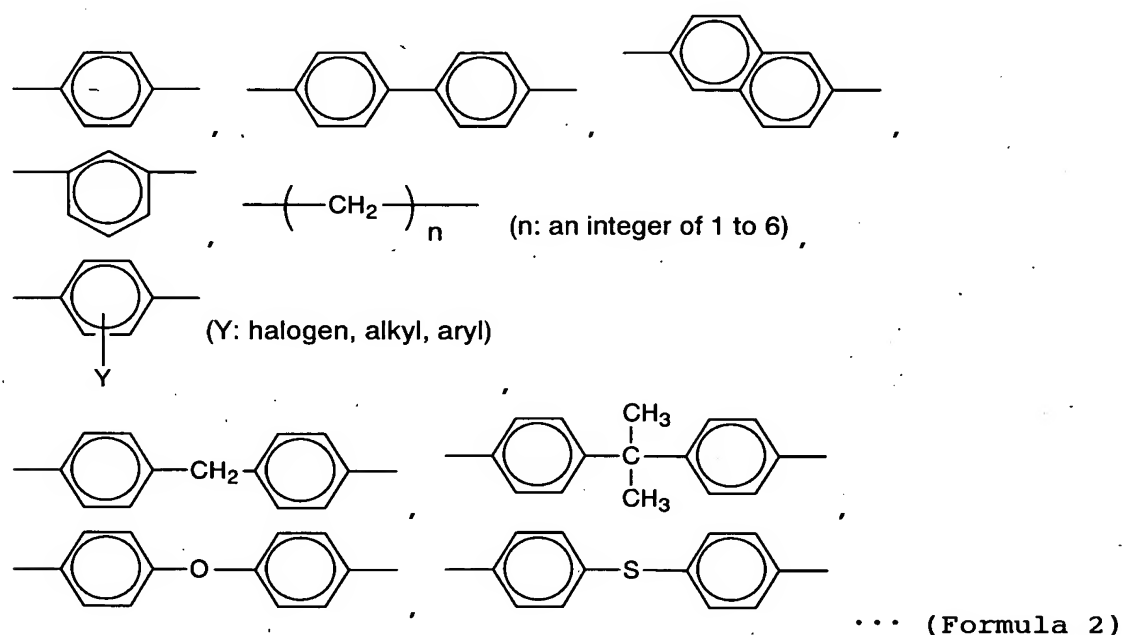


[0019]

In the above-mentioned formulas, structural units (i) and (ii) are structural units of polyester prepared from p-hydroxybenzoic acid and structural units prepared from 2-hydroxy-6-naphthoic acid. Use of these structural units (i) and (ii) makes it possible to obtain a thermoplastic resin composition of the invention having excellent heat resistance and fluidity and being well balanced in mechanical properties such as rigidity. As X in the above-described structural units (iii) and (iv), one or more than one can be selected freely from the following formula (2):

[0020]

[Formula 3]



[0021]

The preferred structural formula (iii) is a structural unit prepared from ethylene glycol, hydroquinone, 4,4'-dihydroxybiphenyl, 2,6-dihydroxynaphthalene or bisphenol A, of which that from ethylene glycol, 4,4'-dihydroxybiphenyl or hydroquinone is more preferred, with that from ethylene glycol or 4,4'-hydroxybiphenyl being particularly preferred. The preferred structural formula (iv) is a structural unit prepared from terephthalic acid, isophthalic acid or 2,6-dicarboxynaphthalene, of which that from terephthalic acid or isophthalic acid is more preferred.

[0022]

As the structural formula (iii) and (iv), the above-mentioned structural units may be used alone or in combination. Specifically, when at least two structural units are used in combination, examples of the

combination for the structural formula (iii) include 1) a structural unit prepared from ethylene glycol/a structural unit prepared from hydroquinone, 2) a structural unit prepared from ethylene glycol/a structural unit prepared from 4,4'-dihydroxybiphenyl, and 3) a structural unit prepared from hydroquinone/a structural unit prepared from 4,4'-dihydroxybiphenyl.
[0023]

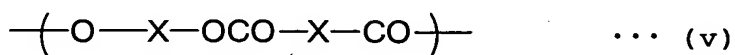
Examples of the combination for the structural formula (iv) include 1) a structural unit prepared from terephthalic acid/a structural unit prepared from isophthalic acid and 2) a structural unit prepared from terephthalic acid/a structural unit prepared from 2,6-dicarboxynaphthalene. In these two components, the amount of terephthalic acid is preferably 40 wt.% or greater, more preferably 60 wt.% or greater, most preferably 80 wt.% or greater. By setting the amount of terephthalic acid at 40 wt.% or greater in the components, the resulting resin composition has relatively good fluidity and heat resistance. Although there is no particular limitation imposed on the ratio of the structural units (i), (ii), (iii) and (iv) in the liquid-crystal polyester component (B), the structural units (iii) and (iv) are used essentially in an equimolar amount.

[0024]

A structural unit (v) comprising structural units (iii) and (iv) can be used as the structural units in the component (B). Specific Examples include 1) a structural unit prepared from ethylene glycol and terephthalic acid, 2) a structural unit prepared from hydroquinone and terephthalic acid, 3) a structural unit prepared from 4,4'-dihydroxybiphenyl and terephthalic acid, 4) a structural unit prepared from 4,4'-dihydroxybiphenyl and isophthalic acid, and 5) a structural unit prepared from bisphenol A and terephthalic acid.

[0025]

[Formula 4]



[0026]

Into the liquid-crystal polyester component (B) of the invention, another structural unit prepared from an aromatic dicarboxylic acid, aromatic diol or aromatic hydrocarboxylic acid can be introduced as needed within a range of a small amount that does not adversely affect the object of the invention. A temperature at which the component (B) starts

indicating a liquid crystal condition in a molten state (which will hereinafter be called "liquid-crystal starting temperature") is preferably 150 to 350°C, more preferably 180 to 320°C. By adjusting the liquid-crystal starting temperature to this range, the resin composition thus obtained has a favorable color tone and is well balanced in heat resistance and moldability.

[0027]

The dielectric dissipation factor ($\tan \delta$) at 25°C and 1 MHz of the liquid-crystal polyester component (B) of the invention is preferably 0.03 or less, more preferably 0.025 or less. The smaller this dielectric dissipation factor, the smaller the dielectric loss, which makes it possible to suppress generation of electronic noise when the resin composition is used as a raw material for electric and electronic parts. Particularly at 25°C in a high-frequency region, that is, in a region of 1 to 10 GHz, the dielectric dissipation factor ($\tan \delta$) is preferably 0.03 or less, more preferably 0.025 or less.

[0028]

The apparent melt viscosity (shear rate: 100/sec at a liquid-crystal starting temperature +30°C) of the liquid-crystal polyester component (B) of the invention is preferably 10 to 3,000 Pa·s, more preferably 10 to 2,000 Pa·s, particularly preferably 10 to 1,000 Pa·s. By adjusting the apparent melt viscosity within this range, the resulting resin composition has preferable fluidity. The thermal conductivity of the component (B) of the invention in the molten state (liquid-crystal condition) is preferably 0.1 to 2.0 W/mK, more preferably 0.2 to 1.5 W/mK, particularly preferably 0.3 to 1.0 W/mK. By adjusting the thermal conductivity in the molten state (liquid-crystal condition) within this range, the injection molding cycle of the resulting resin composition can be made relatively short.

[0029]

In the composition of the invention, the polyphenylene ether resin (A) is added in an amount of 30 to 99 parts by weight, preferably 70 to 99 parts by weight, more preferably 80 to 95 parts by weight. At an amount exceeding 99 parts by weight, the fluidity is lowered, while amounts less than 30 parts by weight unpreferably decrease the heat resistance and increase the specific gravity of the composition.

The liquid-crystal polyester as the component (B) of the invention

is added in an amount of 1 to 70 parts by weight, preferably 1 to 30 parts by weight, more preferably 5 to 20 parts by weight. Amounts exceeding 70 parts by weight increase the specific gravity of the composition and the cost. On the other hand, at amounts less than 1 parts by weight, sufficient fluidity, impact resistance and chemical resistance cannot be obtained.

[0030]

As strength imparting agents, the organic fillers (C) of the present invention include inorganic compounds such as glass fibers, metallic fibers, potassium titanate, carbon fibers, silicon carbide, ceramics, silicon nitride, mica, nepheline syenite, talc, wollastonite, slag fibers, ferrite, glass beads, glass powder, glass balloons, quartz and silica glass. Of these, glass fibers and carbon fibers are preferred for a balance among fluidity, heat resistance and mechanical properties. Glass fibers are more preferred. No limitation is imposed on the shape of such inorganic fillers and free selection from fibrous, plate-type and spherical inorganic fillers is possible. Two or more of the inorganic fillers can be used in combination. If necessary, the inorganic fillers may be provided for use after pretreatment with a coupling agent of the silane type or titanium type.

[0031]

The amount of the inorganic filler (C) is 0.1 to 200 parts by weight, preferably 1 to 100 parts by weight, more preferably 2 to 20 parts by weight, based on 100 parts by weight, in total, of the components (A) and (B). At amounts less than 0.1 parts by weight, it is difficult to achieve sufficient stiffness, heat resistance and impact resistance. On the other hand, at amounts exceeding 200 parts by weight, sufficient fluidity is difficult to be obtained.

In the present invention, another additional component can be added together with the above-described components as needed within an extent that does not impair the characteristics and advantages of the invention. Examples of the additional component include antioxidants, flame retardant (such as organic phosphoric ester compounds, silicon compounds, phosphazene compounds and polyhedral oligomeric silsesquioxane), elastomers, plasticizers (such as oil, low-molecular-weight polyethylene, epoxidized soybean oil, polyethylene glycol and fatty acid esters), flame retardant auxiliary, weather(light)-resistance improvers, nucleating

agents for polyolefin, slip agents, various colorants and mold releasing agents.

[0032]

The resin composition of the invention can be prepared in various manners. For instance, it can be prepared by melt-kneading with heat using a single-screw extruder, twin-screw extruder, roll, kneader, Brabender Plastograph, or Bumbury mixer. Among them, melt-kneading using a twin-screw extruder is most preferred. The temperature at melt-kneading is not particularly limited, but in general can be optionally selected between 150 and 350°C.

The resin composition thus obtained can be molded into various parts in the conventional manner such as injection molding, extrusion molding and blow molding.

[0033]

Such molded products are particularly suitable for applications that require flame retardancy such as heat resistant parts for automobiles and office machines. Examples of the heat resistant parts for automobiles include alternator terminal, alternator connector, IC regulator, potentiometer bases for light dimmers, various valves such as exhaust gas valves, various pipes for fuel, exhaust gas and intake air, air intake nozzle snorkel, intake manifold, fuel pump, joints of engine coolant, carburetor main body, carburetor spacer, exhaust gas sensor, coolant sensor, oil temperature sensor, brake pad wear sensor, throttle position sensor, crank shaft position sensor, air flow meter, brake pad abrasion sensor, thermostat base for air conditioners, flow control valve of hot-air heaters, brush holder for radiator motor, water pump impeller, turbine vane, wiper motor part, distributor, starter switches, starter relay, wire harness for a transmission, window washer nozzle, air conditioner panel switch substrate, coil for fuel-related electric magnetic valves, fuse connector, horn terminal, insulating plate for electrical components, step motor rotor, brake piston, solenoid bobbin, engine oil filter, parts such as an ignition device case, wheel cap, lamp socket, lamp housing, lamp extension and lamp reflector. Among them, the molded products can suitably be applied to lamp extensions and lamp reflectors for balance among lightweightness, heat resistance, flame retardancy and mechanical properties.

[0034]

As the heat resistant parts for office electric machines, parts of household or office electronic appliances typified by parts for an air conditioner, parts of a typewriter and parts of a word processor; office-computer-related parts; telephone-related parts; facsimile-related parts and copying-machine-related parts are preferred.

The present invention will hereinafter be described based on Examples. However, they should not be construed as limiting the scope of the present invention.

[0035]

(Components to be used in Examples)

1. Polyphenylene ether

PPE-1: poly(2,6-dimethyl-1,4-phenylene ether) obtained by oxidation-polymerizing 2,6-dimethylphenol and having reduced viscosity of 0.42, Mw of 34,600 and Mw/Mn of 1.90.

PPE-2: reduced viscosity=0.46, Mw=40,700, Mw/Mn=2.42

PPE-3: reduced viscosity=0.52, Mw=51,900, Mw/Mn=1.95

PPE-4: reduced viscosity=0.51, Mw=48,000, Mw/Mn=2.79

PPE-5: reduced viscosity=0.55, Mw=58,200, Mw/Mn=3.31

PPE-6: reduced viscosity=0.57, Mw=57,900, Mw/Mn=1.88

PPE-7: reduced viscosity=0.39, Mw=43,000, Mw/Mn=2.87

PPE-8: reduced viscosity=0.37, Mw=41,600, Mw/Mn=3.41

[0036]

(Condition for measuring molecular weight)

The molecular weight of polyphenylene ether was determined by using gel permeation chromatography (GPC) ("HL-802 RTS", manufactured by Toyo Soda Co., Ltd.) and a working curve obtained from standard polystyrene samples. For the measurement, there are used standard polystyrene samples having a molecular weight of 264, 364, 466, 568, 2,800, 16,700, 186,000, or 1,260,000, chromatographic columns ("TSK gel G2500H XL", "TSK gel G3000H XL", "TSK gel G4000H XL" and "TSK gel G5000H XL", manufactured by Toyo Soda Co., Ltd.) connected in series and chloroform as a solvent. The measurement is conducted at a solvent flow rate of 0.9 ml/min, and at a temperature of the columns of 40°C. The molecular weights of standard polystyrene and polyphenylene ether are measured using the wavelength of ultraviolet rays of 254 nm and 283 nm, respectively.

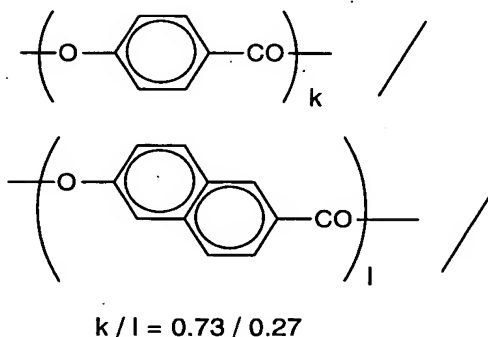
[0037]

Liquid-crystal polyester:

LCP-1: Under a nitrogen atmosphere, p-hydroxybenzoic acid, 2-hydroxy-6-naphthoic acid and acetic anhydride were charged, followed by melting under heat and polycondensation, whereby the liquid-crystal polyester having the below-described theoretical structural formula was obtained. The component ratio of the composition is indicated by a molar ratio.

[0038]

[Formula 5]

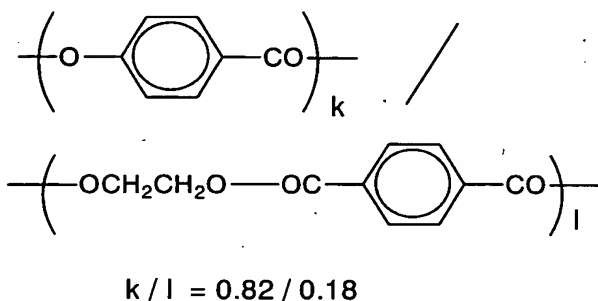


[0039]

LCP-2: Under a nitrogen atmosphere, p-hydroxybenzoic acid, polyethylene terephthalate and acetic anhydride were charged, followed by melting under heat and polycondensation, whereby the liquid-crystal polyester having the below-described theoretical structural formula was obtained. The component ratio of the composition is indicated by a molar ratio.

[0040]

[Formula 6]



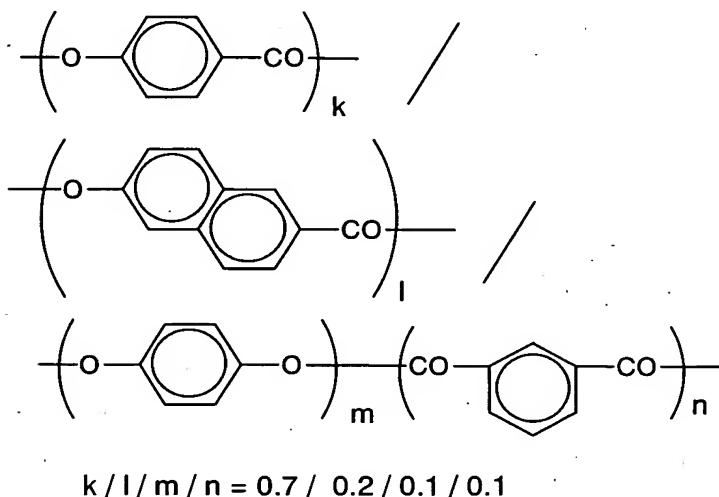
[0041]

LCP-3: Under a nitrogen atmosphere, p-hydroxybenzoic acid,

2-hydroxy-6-naphthoic acid, hydroquinone, isophthalic acid and acetic anhydride were charged, followed by melting under heat and polycondensation, whereby the liquid-crystal polyester having the below-described theoretical structural formula was obtained. The component ratio of the composition is indicated by a molar ratio.

[0042]

[Formula 7]



[0043]

Molding and evaluation of physical properties of each of the resin composition were conducted in the following manners.

(1) Molding

Resultant pellets were molded using an injection molding machine ("IS-80EPN", manufactured by Toshiba Machine Co., Ltd.) set at a cylinder temperature of 330/330/320/310°C, an injection rate of 85% and a mold temperature of 90°C. In Comparative Examples 1 and 3 wherein a strip specimen of 1.6 mm thick was molded, the cavity of a metal mold could not be filled with a molten resin even at an injection pressure of 13 MPa (gage pressure), which was the maximum injection pressure for the machine. Thus, the mold temperature was set at 140°C.

(2) Impact resistance

According to ASTM D256, specimens having a thickness of 3.2 mm were molded. The unnotched Izod impact strength was measured using the resultant specimens. The Izod impact strength is sometimes simply referred to as "Izod".

[0044]

(3) Chemical resistance

An ASTM dumbbell specimen 3.2 mm thick was kept in a solution comprising 60 wt.% of isopropanol and 40 wt.% of cyclohexane for 30 minutes under 0.5 % strain at a temperature of 23°C. The solvent sufficiently evaporated after the specimen was pulled out from the solution, and the tensile strength (TS_1) of the specimen was evaluated at a chuck distance of 115 mm and a test speed of 5 mm/min by using an autograph "AG-5000", manufactured by Shimadzu Corporation). The tensile strength (TS_0) of a specimen not dipped in the solution was evaluated in the same manner. Retention of tensile strength (%) was obtained according to the following equation.

$$\text{Retention of tensile strength (\%)} = TS_1/TS_0 \times 100$$

A larger retention of tensile strength means that the chemical resistance is better.

A broken specimen when pulled out from the solution is shown as "X" in the Tables.

[0045]

(4) Fluidity

At the time when the obtained pellets were injection molded into an ASTM specimen 1.6 mm thick under the condition as described in the above (1), the gauge pressure, at which the resultant specimen was obtained just after being injection molded, being shorter than the cavity by 1 mm in length, was measured. The gauge was assumed as an SSP (abbreviation of "short shot pressure") (MPa). The smaller the SSP, the better the fluidity.

(5) Heat resistance (DTUL)

ASTM strip specimens 3.2 mm thick × 127 mm long × 12.7 mm wide were obtained by molding. According to ASTM D648, the heat distortion temperature of the resultant specimens was measured under a load of 1.82 MPa.

[0046]

(6) Flame retardancy

(Average combustion time)

An ASTM strip specimen 1.6 mm thick × 127 mm long × 12.7 mm wide was obtained by molding and a burning test was conducted based on UL-94 Vertical Burning Test of Underwriters laboratories. This burning test

was conducted on five specimens. Assuming that the time from the removal of a flame after ignition of each specimen therewith for 10 seconds until extinction of the flame is the combustion time t_1 (sec) and the time from the removal of a flame after ignition of the specimens therewith again for 10 seconds until extinction of the flame is the combustion time t_2 (sec), an average combustion time of t_1 and t_2 of each of five specimens were determined.

(Dropping of flaming article)

It was observed whether any flaming article dropped in the burning tests for t_1 and t_2 for each of five specimens (ten tests in total).

O: No dropping observed in all of the ten tests

X: Dropping observed in at least one of the ten tests

[0047]

[Example 1]

Pellets were obtained by melt-kneading the polyphenylene ether (PPE-1) and the liquid-crystal polyester (LCP-1) at a ratio (parts by weight) shown in Table 1 using a twin-screw extruder ("ZSK-25", manufactured by Warner & Pfleiderer Corp.), which was set at 250 to 310°C and was equipped with a vent port. A polymer was precipitated by dissolving a part of the pellets (2 g) in 100 ml of chloroform at room temperature, removing insoluble material by filtration, and charging the resultant solution in a sufficient amount of methanol. Then, a polymer was obtained by washing the precipitated polymer with methanol followed by drying at 140°C under reduced pressure for 1 hour. The molecular weight distribution of the resultant polymer was measured using the GPC and the weight ratio of the polymer having a molecular weight of 20,000 or less was obtained. The results are shown in Table 1. Further, the remained pellets were molded in the manner mentioned above and physical properties of the molded articles were evaluated. The results are shown in Table 1.

[0048]

[Examples 2 to 9]

Each component was mixed at a ratio shown in Table 1, and the same procedure as in Example 1 was conducted. In the table, "HIPS" and "GF" indicates high impact polystyrene ("H9405", manufactured by A & M Styrene Co., Ltd.) and glass fibers ("Microglass RES03-TP30", manufactured by NGF Company), respectively.

[0049]

[Comparative Examples 1 to 3]

Each component was mixed at a ratio shown in Table 1, and the same procedure as in Example 1 was conducted.

[0050]

[Comparative Example 4]

The same procedure as in Example 1 was conducted except that liquid-crystal polyester (LCP-1) was not used.

[0051]

[Table 1]

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Composition	(A)	PPE-1	95			90	93		90				100
		PPE-2											
		PPE-3		93					5				
		PPE-4		90									
		PPE-5			80			70					
		PPE-6								95			
		PPE-7									95		
		PPE-8										95	
		HIPS				5							
	(B)	LCP-1	5	5	7		5		2.5	5	5	5	
Physical Properties		LCP-2						15	2.5				
		LCP-3						15					
	(C)	GF					2	20					
		Weight ratio of polymer with molecular weight of 20,000 or less (%)	16.6	19.1	10.1	21.7	16.4	23.3	16.5	4.2	31.1	34.8	15.5
		Mw/Mn	2.38	2.56	2.23	2.84	2.37	3.29	2.33	2.11	3.12	3.60	2.42
	Impact resistance	Izod (J/m)	1580	1390	1720	1480	1450	1370	1640	1280	509	385	1540
	Chemical resistance	Retention of TS (%)	95	88	100	85	98	95	95	98	X	X	73
	Fluidity	SSP (MPa)	9.6	10	6.8	5.0	6.2	4.9	7.4	>13	6.0	5.4	>13
	Heat resistance	DTUL (°C)	185	184	183	182	186	188	182	185	184	183	185
	Flame retardancy	Average combustion time (sec)	8.0	8.5	7.8	13.5	8.3	8.7	9.9	12.1	15.4	18.8	11.1
			V-1	V-1	V-1	V-1	V-1	V-1	V-1	V-1	V-1	V-2	V-1
		Dropping	O	O	O	O	O	O	O	O	O	X	O

[0052]

[Effect of the Invention]

According to the present invention, it has become possible to provide a polyphenylene ether resin composition which can simultaneously attain excellent impact resistance, chemical resistance, fluidity, heat resistance and flame retardancy, especially very excellent impact resistance chemical resistance and fluidity.

[DOCUMENT NAME] Abstract

[ABSTRACT]

[PROBLEM]

To provide a polyphenylene ether resin composition which can simultaneously attain excellent impact resistance, chemical resistance, fluidity, heat resistance and flame retardancy, especially very excellent impact resistance chemical resistance and fluidity.

[MEANS TO SOLVE THE PROBLEMS]

A resin composition comprising:

(A) 30 to 99 parts by weight of a polyphenylene ether resin, and
(B) 1 to 70 parts by weight of a liquid-crystal polyester,
wherein the polyphenylene ether resin in the composition contains 5 to 30 wt.% of polymer having a molecular weight of 20,000 or less and has a molecular weight distribution (M_w/M_n) of 1.8 to 3.5.

[SELECTED FIGURE] No selected figure


VERIFIED TRANSLATION

I, Rei Terasaki, hereby declare that:

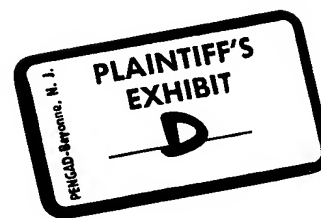
I am knowledgeable in Japanese and English. I have reviewed the attached document and believe it to be an accurate translation of Japanese Patent Application No. 2001-270006 filed on September 6, 2001.

All statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true. Further, these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: Nov. 10, 2003



Rei Terasaki



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[AMOUNT OF PAYMENT] 21,000 yen

[LIST OF MATERIALS TO BE SUBMITTED]

[NAME OF MATERIAL] Specification

[NUMBER OF MATERIAL] 1

[LIST OF MATERIALS TO BE SUBMITTED]

[NAME OF MATERIAL] Abstract

[NUMBER OF MATERIAL] 1

[NECESSITY FOR PROOF] 1: Necessary to prove

[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

A resin composition capable of forming specific morphology

[SCOPE OF PATENT]

[Claim 1]

A resin composition comprising two or more different thermoplastic resins and a zinc compound, wherein the composition is capable of forming morphology comprising a continuous phase and a disperse phase, in which the abundance ratio (R) of Zn in the disperse phase obtained by TEM-EDX is 0.0005 or more and a requirement of $R_d > R_m$ when $R_m = 0$ or $150R_m > R_d > R_m$ when $R_m \neq 0$ (wherein the abundance ratio (R) of Zn = (the number of $L\alpha$ -rays of Zn) / (the number of $K\alpha$ -rays of C), R_d represents R in the disperse phase, and R_m represents R in the continuous phase) is satisfied.

[Claim 2]

The resin composition according to claim 1, wherein the disperse phase mainly comprises a liquid-crystal polyester (a) and the continuous phase mainly comprises a thermoplastic resin (b) being different from the component (a).

[Claim 3]

The resin composition according to claim 1 or 2, wherein the component (b) mainly comprises at least one resin selected from the group consisting of polyphenylene ether resins, polycarbonate, polyester, polyamide, polyacetal, polyphenylene sulfide, polyether imide, polyether sulfone, polyether ketone, polyether etherketone, polystyrene resins, and polyolefin resins.

[Claim 4]

The resin composition according to any one of claims 1 to 3, wherein the component (a) is contained in an amount of 1 to 50 parts by mass and the component (b) is contained in an amount of 99 to 50 parts by mass.

[Claim 5]

The resin composition according to any one of claims 1 to 4, wherein the zinc compound is contained in an amount of 0.001 to 3 parts by mass based on 100 parts by mass, in total, of the components (a) and (b).

[Claim 6]

The resin composition according to any one of claims 1 to 5, wherein the zinc compound is ZnO.

[Claim 7]

The resin composition according to any one of claims 1 to 6, wherein the component (b) is a polyphenylene ether resin.

[Claim 8]

The resin composition according to any one of claims 1 to 7, wherein the component (b) is a polyphenylene ether resin functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride.

[Claim 9]

The resin composition according to claim 8, wherein the polyphenylene ether resin is functionalized with the α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride at a reaction temperature of 210°C or lower in a solid state.

[Claim 10]

The resin composition according to any one of claims 1 to 9, wherein 0.1 to 30 parts by mass of (c) a block copolymer of an aromatic vinyl compound and a conjugated diene compound, which is functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride, and/or a partially hydrogenated block copolymer of an aromatic vinyl compound and a conjugated diene compound, which is functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride, is added based on 100 parts by mass, in total, of the components (a) and (b).

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a resin composition which is capable of forming specific morphology, and which is excellent in impact resistance, especially in dart impact resistance, and at the same time achieves heat resistance, tensile strength and flame retardancy at a high level.

[0002]

[Prior Art]

In general, polyphenylene ethers are resins that have excellent properties of, for example, heat resistance, hot water resistance, size stability, and mechanical and electrical properties, but are accompanied with drawbacks such as poor moldability, i.e., poor fluidity, owing to their high melt viscosity, bad chemical resistance and low impact resistance. With a view to improving such defects of polyphenylene ethers, methods

of alloying polyphenylene ethers with other resins have conventionally been conducted.

[0003]

For example, it is well known that alloying the polyphenylene ethers with polystyrene, high-impact polystyrene or the like improves the fluidity of the compositions. However, there are problems such as deterioration of the flame retardancy and the heat resistance.

While, JP-A-56-115357, for example, proposed a process of mixing polymers such as polyphenylene ether and a liquid-crystal polyester, thereby improving the melt processability of the polyphenylene ether. This process, however, is not sufficient to improve the impact resistance. JP-A-2-97555 proposed a process of mixing a liquid-crystal polyester with various polyallylene oxides in order to improve solder heat resistance, and JP-A-6-122762 proposed a process of mixing an amine-modified polyphenylene ether with a liquid-crystal polyester. Neither process is sufficient for a balance of dart impact resistance, heat resistance, tensile strength and flame retardancy.

[0004]

Further, JP-A-5-117505 and JP-A-9-111103 proposed a process of adding an organic silane coupling agents at the time of alloying polyphenylene ether and a liquid-crystal polyester. However, neither process is sufficient for a balance of dart impact resistance, heat resistance, tensile strength and flame retardancy. JP-A-5-86288 proposed a method for enhancing retention of strength and stiffness upon recycling, but it is not sufficient in impact resistance.

JP-A-4-202462 proposed a process of making polyphenylene ether compatible by adding a polymer containing an epoxy group to improve impact resistance, but it is not sufficient in a balance of dart impact resistance, heat resistance, tensile strength and flame retardancy.

[0005]

[Problems to be Solved by the Invention]

The present invention purposes to provide a resin composition which is capable of forming specific morphology, and which has excellent impact resistance, especially excellent dart impact resistance, and at the same time achieves heat resistance, tensile strength and flame retardancy at a high level.

[0006]

[Means to Solve the Problems]

The present inventors carried out extensive investigations to solve the above problems. As a result, they found that a composition comprising two or more different types of thermoplastic resin and a zinc compound as essential components wherein each resin component is incorporated in a specific ratio could form morphology where existence of Zn atoms is peculiar, and exhibited excellent effects in impact resistance, especially, dart impact resistance. Further, the present inventors found that impact resistance, heat resistance, tensile strength and flame retardancy could be achieved at a high level to accomplish the present invention. Namely, the present invention is as follows:

[0007]

1. A resin composition comprising two or more different thermoplastic resins and a zinc compound, wherein the composition is capable of forming morphology comprising a continuous phase and a disperse phase, in which the abundance ratio (R) of Zn in the disperse phase obtained by TEM-EDX is 0.0005 or more and a requirement of $R_d > R_m$ when $R_m = 0$ or $150R_m > R_d > R_m$ when $R_m \neq 0$ (wherein the abundance ratio (R) of Zn = (the number of $L\alpha$ -rays of Zn) / (the number of $K\alpha$ -rays of C), R_d represents R in the disperse phase, and R_m represents R in the continuous phase) is satisfied.

[0008]

2. The resin composition according to the above 1, wherein the disperse phase mainly comprises a liquid-crystal polyester (a) and the continuous phase mainly comprises a thermoplastic resin (b) being different from the component (a).

3. The resin composition according to the above 1 or 2, wherein the component (b) mainly comprises at least one resin selected from the group consisting of polyphenylene ether resins, polycarbonate, polyester, polyamide, polyacetal, polyphenylene sulfide, polyether imide, polyether sulfone, polyether ketone, polyether etherketone, polystyrene resins, and polyolefin resins.

[0009]

4. The resin composition according to any one of the above 1 to 3, wherein the component (a) is contained in an amount of 1 to 50 parts by mass and the component (b) is contained in an amount of 99 to 50 parts by mass.

5. The resin composition according to any one of the above 1 to 4,

wherein the zinc compound is contained in an amount of 0.001 to 3 parts by mass based on 100 parts by mass, in total, of the components (a) and (b).

6. The resin composition according to any one of the above 1 to 5, wherein the zinc compound is ZnO.

[0010]

7. The resin composition according to any one of the above 1 to 6, wherein the component (b) is a polyphenylene ether resin.

8. The resin composition according to any one of claims 1 to 7, wherein the component (b) is a polyphenylene ether resin functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride.

9. The resin composition according to the above 8, wherein the polyphenylene ether resin is functionalized with the α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic acid anhydride at a reaction temperature of 210°C or lower in a solid state.

[0011]

10. The resin composition according to any one of the above 1 to 9, wherein 0.1 to 30 parts by mass of (c) a block copolymer of an aromatic vinyl compound and a conjugated diene compound, which is functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride, and/or a partially hydrogenated block copolymer of an aromatic vinyl compound and a conjugated diene compound, which is functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride, is added based on 100 parts by mass, in total, of the components (a) and (b).

[0012]

[Embodiment of the Present Invention]

Hereinafter, the present invention is specifically described.

The resin composition used in the present invention are necessary to comprises two or more different types of thermoplastic resins and a zinc compound as an essential components. Further, it can form a morphology, which is observed with a transmission electron microscope (which may hereinafter be called "TEM"), wherein the abundance ratio of element Zn in the disperse phase obtained by using TEM-EDX (which is usually called a "transmission electron microscope-energy dispersive X-ray spectrometer", and which makes it possible to determine the quantity and to identify

the element in each phase upon the TEM observation) is 0.0005 or more and the requirement of $R_d > R_m$ when $R_m = 0$ or $150R_m > R_d > R_m$ when $R_m \neq 0$ is satisfied. The abundance ratio (R) of Zn = (the number of L α -rays of Zn)/(the number of K α -rays of C), wherein R_d represents R in the disperse phase, and R_m represents R in the continuous phase.

[0013]

Herein, the abundance ratio (R) of element Zn is determined in the following manner. Specimens approximately 100 nm thick are prepared by cutting them out from the center of dumbbell specimens that are 3.2 mm thick \times 216 mm long according to the ASTM standard which are obtained by injection molding. They are subjected to TEM observation without staining to count the number of L α -rays of element Zn and K α -rays of element C in the disperse phase and the continuous phase, respectively, with TEM-EDX. In each phase, the numbers of K α -rays and L α -rays counted at 10 different spots are analyzed to obtain an average. In the case of analysis of spots in the disperse phase, the size of the spots is adjusted so as to be smaller than the diameter of the disperse phase. Each average of the numbers is assumed as the number of L α -rays of element Zn and K α -rays of element C. The abundance ratio (R) of Zn is determined by the following formula:

Abundance ratio (R) of Zn =

(the number of L α -rays of Zn)/(the number of K α -rays of C)

[0014]

From the fact that the requirement of $R_d > R_m$ when $R_m = 0$ or $150R_m > R_d > R_m$ when $R_m \neq 0$ is satisfied, it can be said that the feature of the invention is that the disperse phase contains a higher amount of the zinc elements, which are derived from the zinc compound to be added in the composition, than the continuous phase does. Further, it is important that the abundance ratio (R) of the zinc elements existing in the disperse phase is in a specific range. Such an abundance ratio in a specific range is especially effective to improve the dart impact resistance. From the viewpoint of dart impact resistance, the abundance ratio of Zn in the disperse phase is preferably 0.0005 or more, more preferably 0.001 or more. When $R_m = 0$, " $R_d > R_m$ " is preferred. When $R_m \neq 0$, " $150R_m > R_d > R_m$ " is preferred, " $100R_m > R_d > 2R_m$ " is more preferred, and " $50R_m > R_d > 4R_m$ " is most preferred.

[0015]

The zinc compound used in the present invention is a compound

containing zinc elements. Specifically, they include zinc oxide, zinc sulfate, zinc nitrate, zinc chloride, zinc stearate and metallic zinc. And, zinc oxide ZnO is preferably used.

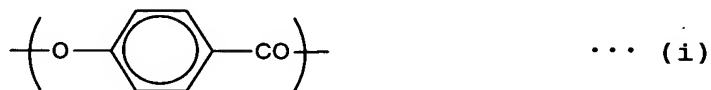
It is preferred that the disperse phase is mainly composed of liquid-crystal polyester (a) and the continuous phase is mainly composed of thermoplastic resin (b) being different from the component (a).

[0016]

As the liquid-crystal polyester (a) of the present invention, known polyesters called "thermotropic liquid-crystal polymers" can be used. Examples thereof include thermotropic liquid-crystal polyesters having, as a main constitutional unit, p-hydroxybenzoic acid and polyethylene terephthalate, thermotropic liquid-crystal polyesters having, as a main constitutional unit, p-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid and thermotropic liquid-crystal polyesters having, as a main constitutional unit, p-hydroxybenzoic acid, 4,4'-dihydroxybiphenyl and terephthalic acid. As the liquid-crystal polymer polyester (a) to be used in the invention, although no particular limitation is imposed on them, those having the following structural units (i) and (ii), and optionally (iii) and/or (iv) are preferred.

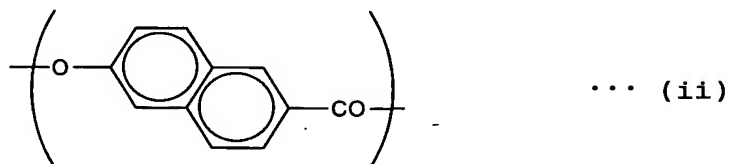
[0017]

[Formula 1]



[0018]

[Formula 2]



[0019]

[Formula 3]



[0020]

[Formula 4]

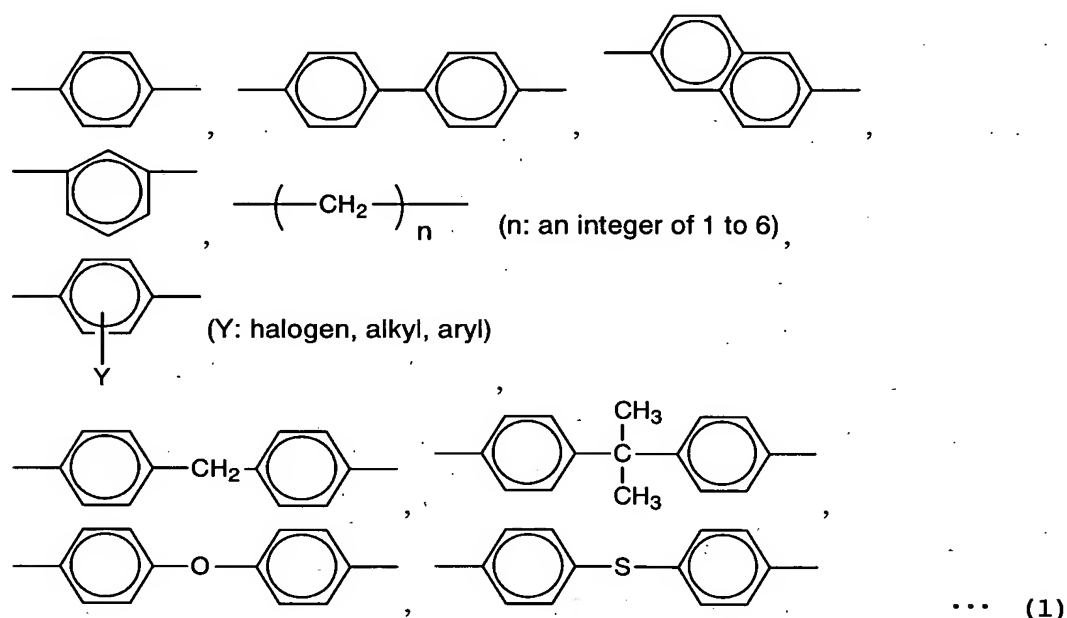


[0021]

In the above formulas, structural units (i) and (ii) are structural units of polyester prepared from p-hydroxybenzoic acid and structural units prepared from 2-hydroxy-6-naphthoic acid, respectively. Use of these structural units (i) and (ii) makes it possible to obtain a thermoplastic resin composition of the invention being well balanced in heat resistance, fluidity and mechanical properties such as rigidity. As X in the above-described structural units (iii) and (iv), one or more than one can be selected freely from the following formula (1):

[0022]

[Formula 5]



[0023]

The preferred structural formula (iii) is a structural unit prepared from ethylene glycol, hydroquinone, 4,4'-dihydroxybiphenyl, 2,6-dihydroxynaphthalene or bisphenol A, of which that from ethylene glycol, 4,4'-dihydroxybiphenyl or hydroquinone is more preferred, with that from ethylene glycol or 4,4'-hydroxybiphenyl being particularly preferred. The preferred structural formula (iv) is a structural unit prepared from terephthalic acid, isophthalic acid or 2,6-dicarboxynaphthalene, of which that from terephthalic acid or isophthalic acid is more preferred.

[0024]

As the structural formula (iii) or (iv), one or more than one structural units exemplified above may be used in combination. More specifically, when at least two structural units are used in combination, examples of the combination for the structural formula (iii) include 1)

a structural unit prepared from ethylene glycol/a structural unit prepared from hydroquinone, 2) a structural unit prepared from ethylene glycol/a structural unit prepared from 4,4'-dihydroxybiphenyl, and 3) a structural unit prepared from hydroquinone/a structural unit prepared from 4,4'-dihydroxybiphenyl.

[0025]

Examples of the combination for the structural formula (iv) include 1) a structural unit prepared from terephthalic acid/a structural unit prepared from isophthalic acid and 2) a structural unit prepared from terephthalic acid/a structural unit prepared from 2,6-dicarboxynaphthalene. In these two components, the amount of terephthalic acid is preferably 40 % by mass or greater, more preferably 60 % by mass or greater, most preferably 80 % by mass or greater. By making the amount of terephthalic acid 40 % by mass or greater in the two components, the resulting resin composition achieves relatively good fluidity and heat resistance. Although there is no particular limitation imposed on the ratio of the structural units (i), (ii), (iii) and (iv) in the liquid-crystal polyester component (a), the structural units (iii) and (iv) are used essentially in an equimolar amount.

[0026]

A structural unit (v) comprising structural units (iii) and (iv) can be used as the structural units in the component (a). Specific examples include 1) a structural unit prepared from ethylene glycol and terephthalic acid; 2) a structural unit prepared from hydroquinone and terephthalic acid, 3) a structural unit prepared from 4,4'-dihydroxybiphenyl and terephthalic acid, 4) a structural unit prepared from 4,4'-dihydroxybiphenyl and isophthalic acid, and 5) a structural unit prepared from bisphenol A and terephthalic acid.

[0027]

[Formula 6]



[0028]

Into the liquid-crystal polyester component (a), another structural unit prepared from an aromatic dicarboxylic acid, aromatic diol or aromatic hydrocarboxylic acid can be introduced as needed within a range of a small amount that does not adversely affect the object of the invention. A temperature at which the component (a) starts indicating a liquid crystal

condition in a molten state (which will hereinafter be called "liquid-crystal starting temperature") is preferably 150 to 350°C, more preferably 180 to 320°C. By adjusting the liquid-crystal starting temperature to this range, the resin composition thus obtained is well balanced in heat resistance and moldability.

[0029]

The dielectric dissipation factor ($\tan \delta$) at 25°C and 1 MHz of the liquid-crystal polyester component (a) is preferably 0.03 or less, more preferably 0.025 or less. The smaller this dielectric dissipation factor, the smaller the dielectric loss, which preferably makes it possible to suppress generation of electronic noise when the resin composition is used as a raw material for electric and electronic parts. Particularly at 25°C in a high-frequency region, that is, in a region of 1 to 10 GHz, the dielectric dissipation factor ($\tan \delta$) is preferably 0.03 or less, more preferably 0.025 or less.

[0030]

The apparent melt viscosity (shear rate: 100/sec at a liquid-crystal starting temperature +30°C) of the liquid-crystal polyester component (a) is preferably 100 to 30,000 Pa·s, more preferably 100 to 20,000 Pa·s, particularly preferably 100 to 10,000 Pa·s. By adjusting the apparent melt viscosity within this range, the resulting resin composition has preferable fluidity.

[0031]

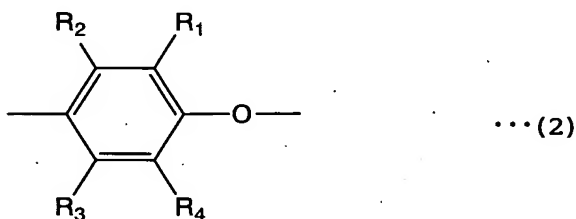
The component (b) used in the present invention is preferably a thermoplastic resin being different from the above-mentioned component (a). Specific examples of the thermoplastic resin include polyphenylene ether resins; polyesters represented by polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polypropylene terephthalate, polycyclohexamethylene terephthalate and the like; polyamides represented by polyamide 6, polyamide 66 and the like; polyacetal; polyphenylene sulfide; polyether imide; polyether sulfone; polyether ketone; polyether ether ketone; polystyrene resins represented by atactic polystyrene, syndiotactic polystyrene, high impact polystyrene, an acrylonitrile-styrene copolymer, an acrylonitrile-butadiene-styrene copolymer, and the like; polyolefin resins represented by low-density polyethylene, high-density polyethylene, polypropylene, polymethyl

pentene, polycycloolefin and the like; and the like. These resins are used alone or in combination. Among them, the polyphenylene ether resins are preferred in view of dart impact resistance, heat resistance, tensile properties and flame retardancy.

The polyphenylene ether resin used in the present invention is a homopolymer and/or a copolymer comprising a recurring unit structure represented by the following formula (2):

[0032]

[Formula 7]



[0033]

(wherein R_1 and R_4 each independently represents hydrogen, primary or secondary lower alkyl, phenyl, aminoalkyl or hydrocarbon oxy; and R_2 and R_3 each independently represents hydrogen, primary or secondary lower alkyl or phenyl), and

having a reduced viscosity (as measured under the condition: 0.5 g/dl, chloroform solution, and 30°C) of preferably 0.15 to 1.0 dl/g. The reduced viscosity is more preferably within a range of 0.20 to 0.70 dl/g, most preferably within a range of 0.40 to 0.60 dl/g.

[0034]

Specific examples of the polyphenylene ether resin include poly(2,6-dimethyl-1,4-phenylene ether), poly(2-methyl-6-ethyl-1,4-phenylene ether), poly(2-methyl-6-phenyl-1,4-phenylene ether), poly(2,6-dichloro-1,4-phenylene ether), and the like. Further, the polyphenylene ether copolymers such as copolymers of 2,6-dimethylphenol and another phenol (such as 2,3,6-trimethylphenol or 2-methyl-6-butylphenol) are also usable. Among them, poly(2,6-dimethyl-1,4-phenylene ether) and a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol are preferred, of which the poly(2,6-dimethyl-1,4-phenylene ether) is more preferred.

[0035]

Examples of a manufacturing process of the polyphenylene ether resin

to be used in the present invention include the process described in U.S. Patent No. 3,306,874 wherein 2,6-xylenol is subjected to oxidation polymerization in the presence of a complex comprising a cuprous salt and an amine as a catalyst. The process described in U.S. Patent Nos. 3,306,875, 3,257,357 and 3,257,358, JP-B-52-017880, JP-A-50-51197 and JP-A-63-152628 are also preferred as a manufacturing process of the polyphenylene ether resin.

The polyphenylene ether resin may be used in the form of a powder after polymerization or in the form of pellets produced by melt kneading the powder of polyphenylene ether resin with an extruder in the atmosphere of an N₂ gas or non-N₂ gas with or without deaeration.

[0036]

The polyphenylene ether resin is preferably functionalized by the following functionalizing compound in view of the dart impact resistance. That is, a functionalizing compound herein is preferably compounds having unsaturated bonds, especially double bonds. Specific examples of the functionalizing compound include maleic anhydride, maleic acid, fumaric acid, phenyl maleimide, itaconic acid, acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, glycidyl acrylate, glycidyl methacrylate, stearyl acrylate and styrene. Further, from the viewpoint of the dart impact resistance, α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride is preferable. Further specifically, maleic acid, fumaric acid or maleic anhydride is exemplified. Particularly, maleic anhydride is more preferably used.

[0037]

As the method for functionalization with these functionalizing compounds, functionalizing the polyphenylene ether in a molten state in the presence or absence of a radical generator by using an extruder, with or without deaeration, can be exemplified. In view of the impact resistance, it is preferable to functionalize the polyphenylene ether in a non-molten state (i.e., in a solid state at a temperature between room temperature and melting point), in the presence or absence of a radical generator. Upon functionalization, the melting point of the polyphenylene ether is determined by the top temperature of the peak in a temperature-heat quantity graph, which is observed at the measurement with a differential scanning calorimeter (DSC) wherein the temperature increases at 20°C/min. In case where plural top temperatures in the peaks are observed, the highest

temperature is regarded as the melting point of the polyphenylene ether. Further, it is more preferable that the polyphenylene ether is functionalized in a solid state within the temperature range of the glass transition temperature 210°C or less in view of the impact resistance.

[0038]

Further, the polyphenylene ether resin may contain an aromatic vinyl polymer, if necessary, within an extent which does not damage the characteristics and advantages of the invention. Examples of the aromatic vinyl polymer include polystyrene, high impact polystyrene, an acrylonitrile-styrene copolymer, and the like.

The component (c) used in the present invention is a block copolymer of an aromatic vinyl compound and a conjugated diene compound, which is functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride, and/or a partially hydrogenated block copolymer of an aromatic vinyl compound and a conjugated diene compound, which is functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride. Namely, a block copolymer of an aromatic vinyl compound and a conjugated diene compound is a polymer functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride, and a partially hydrogenated block copolymer of an aromatic vinyl compound and a conjugated diene compound is a polymer functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride. The copolymers may be used alone or in combination. Further, the block copolymer of the aromatic vinyl compound and the conjugated diene compound herein indicates a block copolymer comprising a polymer block segment having aromatic vinyl compounds as a main component and a block polymer segment having conjugated diene compounds as a main component.

[0039]

Specific examples of the aromatic vinyl compound include styrene, α -methyl styrene, vinyl toluene, p-tert-butyl styrene, divinyl benzene, p-methyl styrene, and 1,1-diphenyl styrene, from which at least one can be selected. Among them, styrene is preferred. Specific examples of the conjugated diene compound include butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, piperylene, 3-butyl-1,3-octadiene, and phenyl-1,3-butadiene, from which at least one can be selected. Among them, butadiene and isoprene or a combination thereof are preferred.

[0040]

Further, specific examples of the functionalizing compound such as α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride herein include maleic acid, fumaric acid or maleic anhydride. Particularly, maleic anhydride is more preferably used.

Moreover, functionalization of the copolymer with these functionalizing compounds may be conducted by melt-kneading them in the presence or absence of a radical generator using an extruder or reacting them in a solution.

[0041]

Further, the component (c) is preferably a polymer prepared by partially hydrogenating a block copolymer of an aromatic vinyl compound and a conjugated diene compound and functionalizing the partially hydrogenated block copolymer with the above functionalizing compounds from the viewpoint of heat resistance and heat deterioration resistance. A hydrogenation rate of 5 to 100 % is preferred. A hydrogenation rate of 50 % or more is more preferred for heat stability. Partially hydrogenated block copolymers which have structural characteristics satisfying requirements as precisely described in JP-A-61-34049 can be used individually or in combination. Specific examples of the partially hydrogenated block copolymers include commercially available polymers such as "TaftecTM" sold by Asahi Kasei Corp. Specific examples of the polymers prepared by functionalizing the partially hydrogenated block copolymer with the functionalizing compounds include commercially available polymers such as "Taftec M SeriesTM" sold by Asahi Kasei Corp. The functionalization rate (defined by mass fraction of the functionalizing compound and the partially hydrogenated block copolymer) is preferably 0.1 to 10 %, more preferably 0.3 to 5 %. When the functionalization rate is less than 0.1 %, dart impact resistance is not sufficiently improved. When it is more than 10 %, heat resistance is unpreferably reduced.

[0042]

The amount of (a) the liquid-crystal polyester used in the present invention is 1 to 50 parts by mass, preferably 2 to 40 parts by mass, more preferably 3 to 20 parts by mass. When the amount is more than 50 parts by mass, sufficient impact resistance cannot be achieved. When it is less than 1 part by mass, sufficient fluidity cannot be achieved.

The amount of (b) the thermoplastic resin being different from the

component (a) used in the present invention is 99 to 50 parts by mass, preferably 98 to 60 parts by mass, more preferably 97 to 80 parts by mass. The amount of more than 99 parts by mass lowers the fluidity. The amount of less than 1 part by mass does not achieve sufficient tensile property and appearance.

[0043]

The amount of the zinc compound used in the present invention is 0.001 to 3 parts by mass, preferably 0.01 to 2 parts by mass, more preferably 0.1 to 1 part by mass, based on 100 parts by mass, in total, of the components (a) and (b). When the amount is less than 0.001 part by mass, sufficient dart impact resistance is difficult to be exhibited. The amount of more than 3 parts by weight causes only increase of specific gravity.

[0044]

The amount of the component (c) used in the present invention, the block copolymer of the aromatic vinyl compound and the conjugated diene compound, which is functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride, and/or the partially hydrogenated block copolymer of the aromatic vinyl compound and the conjugated diene compound, which is functionalized with α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic anhydride, is preferably 0.1 to 30 parts by mass, more preferably 0.2 to 10 parts by mass, furthermore preferably 0.5 to 5 parts by mass, based on 100 parts by mass, in total, of the components (a) and (b). The amount of less than 0.1 part by mass is difficult to exhibit sufficient dart impact resistance. The amount of more than 30 parts by mass decreases heat resistance and flame retardancy.

[0045]

In the present invention, another additional component can be added together with the above-described components as needed within an extent that does not impair the characteristics and advantages of the invention. Examples of the additional component include antioxidants, flame retardants (e.g., an organic phosphoric ester compound, an inorganic phosphoric compound and an aromatic halogen flame retardant), elastomers (e.g., an ethylene/propylene copolymer, an ethylene/1-butene copolymer, an ethylene/propylene/non-conjugated diene copolymer, an ethylene/ethyl acrylate copolymer, an ethylene/glycidyl methacrylate copolymer, an ethylene/vinyl acetate/glycidyl methacrylate copolymer, an ethylene propylene-g-maleic anhydride copolymer, olefin copolymers such as ABS,

polyester polyether elastomer, polyester polyester elastomer, a non-functionalized vinyl aromatic compound-conjugated diene block copolymer, and a hydrogenated product of the non-functionalized vinyl aromatic compound-conjugated diene block copolymer), plastisizers (e.g., oil, low-molecular-weight polyethylene, epoxydized soybean oil, polyethylene glycol and fatty acid esters), flame retardant auxiliaries, weather(light)-resistance improvers, slip agents, various colorants and mold releasing agents. Further, inorganic fillers may be added as needed within an extent that does not impair the characteristics and advantages of the invention. Herein, the inorganic fillers include glass fibers, carbon fibers, whisker, mica, talc, carbon black, titanium oxide, calcium carbonate, potassium titanate, wollastonite, electroconductive metallic fibers, electroconductive carbon black, and the like. Of these, glass fibers are preferable. Fibrous fillers such as glass fibers may be coated or bundled with thermoplastic resins such as an ethylene/vinyl acetate copolymer or thermoset resins such as an epoxy resin.

[0046]

The resin composition of the invention can be prepared in various manners. For instance, it can be prepared by melt-kneading with heat using a single-screw extruder, twin-screw extruder, roll, kneader, Branbender Plastograph, or Banbury mixer. Among them, melt-kneading using a twin-screw extruder is most preferred. Upon melt-kneading, the temperature is not particularly limited, and it can be freely selected from 150 to 350°C in general.

The thus-obtained resin composition of the present invention can be molded into various parts in the conventional manner such as injection molding, extrusion molding and blow molding. Particularly, the injection molding is a very suitable molding method since the component (a) of liquid-crystal polyester is more easily formed into fibrils due to high shearing force of the injection molding. These various parts are suitable for, for example, automobile parts and consumer-electric and office automation parts represented by electric and electronic parts.

[0047]

The present invention will be hereinafter described based on Examples. However, they should not be construed as limiting the scope of the present invention.

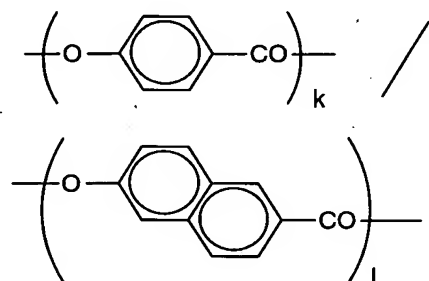
(Preparation Example 1)

Preparation example of liquid-crystal polyester (LCP-1)

Under a nitrogen atmosphere, p-hydroxybenzoic acid, 2-hydroxy-6-naphthoic acid and acetic anhydride were melt under heat and polycondensed to obtain a liquid-crystal polyester (LCP-1) having the below described theoretical structural formula. The component ratio of the composition is indicated by a molar ratio.

[0048]

[Formula 8]



$$k/l = 0.73/0.27$$

[0049]

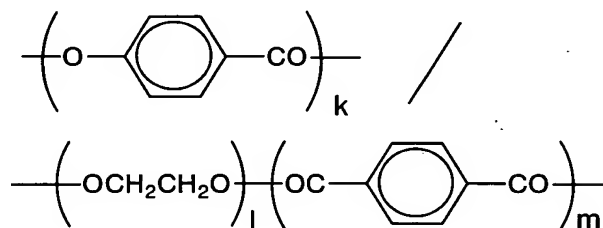
(Preparation Example 2)

Preparation example of liquid-crystal polyester (LCP-2)

Under a nitrogen atmosphere, p-hydroxybenzoic acid, polyethylene terephthalate and acetic anhydride were melted under heat and polycondensed to obtain a liquid-crystal polyester (LCP-2) having the below described theoretical structural formula. The component ratio of the composition is indicated by a molar ratio.

[0050]

[Formula 9]



$$k/l/m = 0.82/0.18/0.18$$

[0051]

(Preparation Example 3)

Preparation example of functionalized polyphenylene ether (PPE-1)

Poly(2,6-dimethyl-1,4-phenylene ether) having a reduced viscosity

of 0.42 prepared by oxidation-polymerizing 2,6-dimethylphenol was used as a raw polyphenylene ether.

0.5 kg of maleic anhydride was fed into an autoclave vessel. The vessel was connected with Henschel mixer FM10C/I manufactured by Mitsui Mining Co., Ltd. through a pipe. 2 kg of raw polyphenylene ether powder was fed in the Henschel mixer and stirred at 600 rpm while substituting the inside of the vessel by nitrogen air. Then, an oil at 200°C was charged in the jacket of the mixer and heated until the raw polyphenylene ether powder reached 190°C.

On the other hand, the autoclave vessel was put in an oil bath to adjust the temperature of maleic anhydride in the vessel at 190°C. At the point when the temperatures of raw polyphenylene ether powder and maleic anhydride were stabilized at 190°C, nitrogen was fed in the direction from the autoclave vessel to the Henschel mixer at 1 L/min and a mixed gas comprising maleic anhydride and nitrogen was transferred to the Henschel mixer. At this time, a valve of a nitrogen discharge port of the Henschel mixer was released so as for the maleic anhydride-nitrogen mixed gas to flow continuously. Under this condition, stirring and flowing of gas were continued for 20 minutes. 20 minutes later, oil having a temperature of 200°C was discharged from the jacket of the apparatus, and in exchange oil at room temperature was charged to cool the polyphenylene ether powder in the mixer down to room temperature. The resultant polyphenylene ether powder was subjected to extraction operation with heat acetone to remove unreacted maleic anhydride so that functionalized polyphenylene ether (PPE-1) was obtained. The added amount of maleic anhydride, which was obtained by titration, was 0.56 parts by mass.

[0052]

(Preparation Example 4)

Preparation example of polyphenylene ether (PPE-2)

2,6-dimethylphenol was oxidation-polymerized to prepare poly(2,6-dimethyl-1,4-phenylene ether) having a reduced viscosity of 0.43.

Molding and evaluation of physical properties of each of the resin compositions were conducted in the following manners.

(1) Molding

The resultant pellets were molded using an injection molding machine ("IS-80EPN", manufactured by Toshiba Machine Co., Ltd.) set at cylinder

temperature of 330/330/320/310°C, an injection rate of 85% and a mold temperature of 90°C.

[0053]

(2) Abundance ratio of Zn

According to the molding manner described in the above (1), dumbbell bars 3.2 mm thick × 216 mm long, based on the ASTM standard, were prepared by injection molding. Specimens having a thickness of 100 nm were obtained by cutting out from the center of the dumbbell bar in the flow direction with an ultramicrotome. The specimens without staining were analyzed at a TEM acceleration voltage of 100 kV with a transmission electron microscope ("JEM-2010", manufactured by JEOL Ltd.). As an EDX apparatus, "VANTAGE DS 400x" (manufactured by Noran Instruments Corp.) was used. The analysis was continued at a TEM acceleration voltage of 200 kV until the number of $CK\alpha$ -rays exceeded 430,000. In the disperse phase and the continuous phase, the number of the $L\alpha$ -rays of element Zn and the $K\alpha$ -rays of element C was counted using TEM-EDX. An average number was obtained by analyzing 10 different spots in each phase. When the spots in the disperse phase were analyzed, the size of the spots was adjusted to be smaller than the diameter of the disperse phase. The average numbers are taken for the number of $L\alpha$ -rays of element Zn and $K\alpha$ -rays of element C. The abundance ratio (R) of Zn was obtained according to the following equation:

[0054]

Abundance ratio (R) of Zn =

(the number of $L\alpha$ -rays of Zn)/(the number of $K\alpha$ -rays of C)

In the equation, R_d represents R in the disperse phase, and R_m represents R in the continuous phase. In the Tables, specimens satisfying the requirement of $R_d > R_m$ when $R_m = 0$ or $150R_m > R_d > R_m$ when $R_m \neq 0$ is defined as "O", and specimens not satisfying the requirements of $R_d > R_m$ when $R_m = 0$ or $150R_m > R_d > R_m$ when $R_m \neq 0$ is defined as "X".

[0055]

(3) Impact resistance (Dart impact and reproducibility of ductile fracture)

The resultant pellets were molded into specimens in the shape of a flat plate 2.5 mm thick × 100 mm long × 50 mm wide under the molding conditions described in the above (1). Measurement of the specimens was conducted under the conditions of a dropping load of 6.5 kg and drop height of 100 cm by using a dart impact tester (manufactured by Toyo Seiki Co.,

Ltd.), and the whole absorption energy, i.e., the sum of cracking energy and propagation energy upon fracture, was designated as a dart impact (J). The greater the dart impact, the better the impact resistance. When the plate specimen was observed from a thickness direction after the fracture test, a ductile fracture was defined as a state where deformation occurred as if the specimen had been hammered thin at the place where the dart was dropped. A brittle fracture was defined as a state where complete gouging occurred at the place where the dart was dropped but the test piece remained flat without deformation. Based on the above-described standards, the ductile fracture was judged. The test was conducted five times (test number (n) = 5).

O: Ductile fracture occurred in all of the five tests.

Δ: Ductile fracture occurred 1 to 4 times out of the five tests, while brittle fracture occurred in the rest of the tests.

X: Brittle fracture occurred in all of the five tests.

[0056]

(4) Heat resistance (Deflection temperature under load)

The resultant pellets were molded into an ASTM strip specimen 3.2 mm thick under the molding conditions described in the above (1). Using the resultant specimen, the heat distortion temperature was measured under a load of 1.82 MPa.

(5) Tensile properties

A tensile test of an ASTM dumbbell specimen 3.2 mm thick was conducted at a chuck distance of 115 mm and a test speed of 20 mm/min by using an autograph ("AG-5000", manufactured by Shimadzu Corporation), whereby the breaking extension (%) was measured.

[0057]

(6) Flame retardancy

An ASTM strip specimen 1.6 mm thick × 127 mm long × 12.7 mm wide was obtained by molding and a burning test was conducted based on the UL-94 Vertical Burning Test of Underwriters Laboratories. This burning test was conducted on five specimens. Assuming that the time from the removal of a flame after ignition of each specimen therewith for 10 seconds until extinction of the flame is the combustion time t_1 (sec) and the time from the removal of a flame after ignition of the specimen therewith again for 10 seconds until extinction of the flame is the combustion time t_2 (sec), an average combustion time of t_1 and t_2 of each of five specimens

was determined. Further, according to the UL-94 standards, the specimens were determined as V-0, V-1 or V-2.

[0058]

[Examples 1 to 4 and Comparative Example 2]

Pellets were obtained by melt-kneading the liquid-crystal polyester (LCP-1), the polyphenylene ether (PPE-1) and zinc oxide as a zinc compound (JIS special grade, manufactured by Wako Pure Chemical Industries, Ltd.; referred to as ZnO in the Table) at a ratio shown in Table 1 using a twin-screw extruder with a vent port ("ZSK-25", manufactured by Werner & Pfleiderer Corp.), which was set at 270 to 310°C. The resultant pellets were molded according to the manner mentioned above and physical properties of the molded articles were evaluated. The results are shown in Table 1.

[0059]

[Comparative Example 1]

Pellets were obtained according to the same manner as in Example 1 except that zinc oxide was not used. The resultant pellets were molded in the manner mentioned above and physical properties of the molded articles were evaluated. The results are shown in Table 1.

[0060]

[Comparative Example 3]

An experiment was conducted in the same manner as in Example 4 except that the components were incorporated at the ratio as shown in Table 1. However, pellets could not be obtained because of considerably inconstant size of strands, i.e., the diameter of strands extruded from the die of the extruder became sometimes thick and sometimes thin. As the result, evaluation could not be conducted.

[0061]

[Examples 5 and 6]

Pellets were obtained according to the same manner as in Example 1 except that polyphenylene ether (PPE-2) was used instead of polyphenylene ether (PPE-1), maleic anhydride block copolymer ("Tuftec™ M1911" manufactured by Asahi Kasei Corp., referred to as "m-SEBS" in the Table) was added, and each component was incorporated at the ratio shown in Table 1. The resultant pellets were molded in the manner mentioned above and physical properties were evaluated. The results are shown in Table 1.

[0062]

[Example 7]

Pellets were prepared according to the same manner as in Example 1 except that maleic anhydride block copolymer was not used. The resultant pellets were molded in the manner mentioned above and physical properties were evaluated. The results are shown in Table 1.

[0063]

[Comparative Example 4]

Pellets were prepared according to the same manner as in Example 5 except that zinc oxide was not used. The resultant pellets were molded in the same manner mentioned above and physical properties were evaluated. The results are shown in Table 1.

[0064]

[Example 8]

Pellets were prepared according to the same manner as in Example 1 except that LCP-1 and LCP-2 were used together as liquid polyester and each component was incorporated at the ratio shown in Table 1. The resultant pellets were molded in the manner mentioned above and physical properties were evaluated. The results are shown in Table 1.

[0065]

[Table 1]

	Ex. 1	Comp. Ex. 1	Ex. 2	Comp. Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 3*	Ex. 5	Ex. 6	Ex. 7	Comp. Ex. 4	Ex. 8
(a)	5	5	5	5	20	45	52	5	5	5	5	2.5
LCP-1												2.5
LCP-2												
(b)	95	95	95	95	80	55	48					95
PPE-1								95	95	95	95	
PPE-2								1	10		1	
(c)												
m-SEBS												
Zinc compound	0.23		4	4	0.4	0.4	0.4	0.8	0.8	0.23		0.15
ZnO												
Abundance ratio of Zn	0.0023	0	0.035	0.004	0.0025	0.0019	-	0.0070	0.0072	0.0019	0	0.0013
R (Rd) in dispersed phase												
R (Rm) in continuous phase	0	0	0.0002	0	0.0001	0.0001	-	0	0.0002	0.0004	0	0
(when Rm = 0)	○	X	-	○	-	-	-	○	-	-	X	○
(when Rm ≠ 0)	-	-	X	-	○	○	-	-	○	○	-	-
150 Rm > Rd > Rm												
Impact resistance	48	7.4	8.3	50	43	39	-	55	53	24	6.6	29
Dart impact (J)												
Reproducibility of ductile fracture (%)	○	X	X	○	○	○	-	○	○	△	X	△
Heat resistance	184	185	185	185	183	181	-	180	173	184	182	182
Heat distortion temperature (°C)												
Tensile properties	65	36	9	60	49	44	-	56	73	49	23	45
Breaking extension (%)												
Flame retardancy	V-1	V-1	V-2	V-1	V-0	V-0	-	V-1	V-1	V-1	V-1	V-1
UL standard												

*Not being kneaded by an extruder

[0066]

As seen from Table 1, existence of Zn in the disperse phase is important to the dart impact property and abundance ratio of Zn in the disperse phase is important to be larger than that in the continuous phase. Further, it is important to the balance of dart impact resistance, heat resistance, tensile properties, and flame retardancy that the abundance ratios in the disperse and continuous phases are in a specific range.

[0067]

[Effects of the Invention]

According to the present invention, there has been achieved a resin composition which is capable of forming specific morphology and which is excellent in impact resistance, especially in dart impact resistance, and at the same time achieves heat resistance, tensile strength and flame retardancy at a high level.

[NAME OF DOCUMENT] Abstract

[ABSTRACT]

[PROBLEM]

To provide a resin composition which is capable of forming specific morphology and which is excellent in impact resistance, especially in dart impact resistance, and at the same time achieves heat resistance, tensile strength and flame retardancy at a high level.

[MEANS TO SOLVE]

A resin composition comprising two or more different thermoplastic resins and a zinc compound, wherein the composition is capable of forming morphology comprising a continuous phase and a disperse phase, in which the abundance ratio (R) of Zn in the disperse phase obtained by TEM-EDX is 0.0005 or more and a requirement of $R_d > R_m$ when $R_m = 0$ or $150R_m > R_d > R_m$ when $R_m \neq 0$ (wherein the abundance ratio (R) of Zn = (the number of $L\alpha$ -rays of Zn) / (the number of $K\alpha$ -rays of C), R_d represents R in the disperse phase, and R_m represents R in the continuous phase) is satisfied.

[SELECTED FIGURE]

. No selected figure.